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EDITORS

DR. L. H. AHRENS, *Department of Geology and Mineralogy, The University, Oxford, England.*

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PROF. L. R. WAGER, F.R.S., *Department of Geology and Mineralogy, The University, Oxford, England.*

PROF. F. E. WICKMAN, *Naturhistoriska Riksmuseets, Mineralogiska Avdelning, Stockholm 50, Sweden.*

VOLUME 8, NOS. 1/2 AUGUST, 1955

CONTENTS

PAGE

L. H. AHRENS: Implications of the Rhodesia age pattern 1

H. A. SHILLIBEER and R. D. RUSSELL: The argon-40 content of the atmosphere and the age of the earth 16

I. I. CHEBOTAREV: Metamorphism of natural waters in the crust of weathering. Part I 22

H. BORCHERT: Die häufigsten Elemente im Durchschnitt der Eruptivgesteine . . 49

R. L. MILLER and EDWARD D. GOLDBERG: The normal distribution in geochemistry 53

IRVING A. BREGER: Radioactive equilibrium in ancient marine sediments . . 63

J. A. S. ADAMS: The uranium geochemistry of Lassen Volcanic National Park, California 74

VINCENT A. SAULL: Chemical energy and metamorphism 86

Announcements. 108

In Memoriam 108

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Implications of the Rhodesia age pattern

L. H. Ahrens
Department of Geology and Mineralogy, Oxford University

(*Received* 31 *May* 1955)

ABSTRACT

An assumption that most published lead age distributions (usually $t(\frac{207}{206})^* > t(\frac{207}{235}) > t(\frac{206}{238})$) are participants of age patterns of the Rhodesia type points to the conclusion that the majority of all recommended lead ages, including $\frac{207}{206}$* estimates, are underestimates. The extent of underestimation should depend in the first place on the degree of internal disagreement, and secondly on which age ($t(\frac{207}{206})$, $t(\frac{207}{235})$ or other) had been recommended. The net effect is a distinct expansion of the lead age scale as a whole.

For specimens participating in the Rhodesia pattern,

$$\log t\left(\frac{206}{238}\right) = at\left(\frac{207}{235}\right) + b$$

where t = age and a and b are constants; several specimens of Witwatersrand uraninite appear to participate in a similar relationship. For atomic ratios rather than calculated ages, the relationship

$$\frac{N_{207}}{N_{235}} = a' \frac{N_{206}}{N_{238}} - b'$$

appears to hold (N = number of atoms).

Varying lead deficiency has been suggested as the cause of the Rhodesia pattern, and the sign of constant b' above and in an equation involving $\frac{N_{208}}{N_{232}}$ indicates a lead isotope deficiency order of 208 > 207 > 206. A deficiency of 207 > 206 is the reverse of that indicated by the age relationship of $t(\frac{207}{235}) > t(\frac{206}{238})$. The apparent anomaly is due to the nature of the age equation itself and to the fact that (i) the half-life of U^{235} is much less than the half-life of U^{238} and (ii) because the deficiency of 207 is not very much greater than that of 206.

Introduction

A previous communication (Ahrens, 1955a) directed attention to a regular lead age pattern (the Rhodesia age pattern—Fig. 1) produced by the age distributions of three specimens of Rhodesian monazite, one Madagascan monazite, and one Manitoban uraninite. It was suggested that the age of each participant of this pattern was precisely the same, and that this age (2680×10^6 years), the convergent age, was given by the point of convergence (Fig. 1). It was concluded further that, following Holmes' suggestion, varying lead loss† had brought about the development of the age pattern, and that the high degree of order in the whole age array pointed to physical control rather than some chemical effect (leaching, etc.). The Rhodesia pattern is examined further in this paper together with a Witwatersrand age pattern, and an attempt will be made to assess the implications of the suggested interpretation of these age patterns on the validity of all published individual lead ages as well as on the lead age scale as a whole as a measure of geological time; a final section is devoted to a brief discussion on the use of the Rhodesia pattern as a guide to finding the actual cause of lead age distributions in general.

---

* Abbreviations $\frac{207}{206}$, $\frac{207}{235}$, etc. will be used in place of $\frac{Pb^{207}}{Pb^{206}}$, $\frac{Pb^{207}}{U^{235}}$, etc.

† Or lead deficiency—see discussion at the end of this paper.

Many published $\frac{208}{232}$ ages, particularly of Th-low minerals, are evidently unsatisfactory, because of faulty analyses and uncertainty of correction for primary lead. Accordingly, for the purposes of this paper, it has seemed wisest to omit $\frac{208}{232}$ ages as a whole, with the exception of those of monazites which are participants of the Rhodesia age pattern; their analyses appear to be satisfactory, and the specimens in any case form a very useful group.

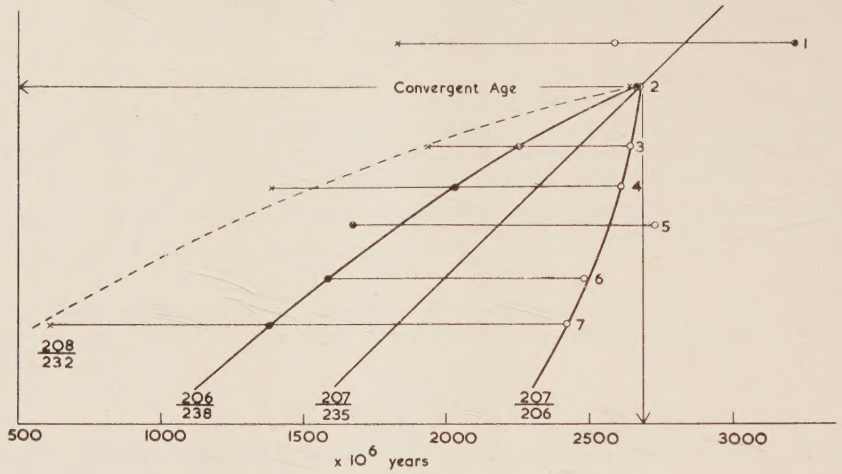

Fig. 1. The Rhodesia age pattern, obtained by relating $t(\frac{207}{235})$ as ordinate vs. $t(\frac{206}{238})$, $t(\frac{208}{232})$, and $t(\frac{207}{206})$. Age equality is indicated by the straight line of unit slope which may also be used to read $t(\frac{207}{235})$ on the abscissa.
1—monazite (Huron Claim, S-E Manitoba); 2, 3, and 4—monazites (Ebonite, Jack Tin, and Irumi, Rhodesia—for details see HOLMES, 1954); 5—uraninite (Huron Claim, S-E Manitoba) and 6—monazite (Antsirabe, Madagascar).

THE RHODESIA AND WITWATERSRAND AGE PATTERNS

In arriving at the conclusion that the convergent age is the true lead age for all participants of the Rhodesia age pattern, we reason as follows. From geological considerations the reasonable assumption is first made that each Rhodesia specimen is of the same age; in one specimen (Ebonite) all ages are in general agreement (Fig. 1) and this age is assumed to be correct. In the other two specimens, significant internal disagreement is found ($t(\frac{207}{206}) > t(\frac{207}{235}) > t(\frac{206}{238}) > t(\frac{208}{232})$), but in varying degree, and the age distributions are such that they form a well-ordered, convergent age-pattern, with the ages of the Ebonite specimen concentrated at the point of convergence; the formation of such an age-pattern is, in itself, indirect support of an assumption of age equality. The age distributions of Manitoban uraninite and Madagascan monazite fit an extension of the Rhodesia pattern precisely, and hence for them too the point of convergence for the pattern as a whole is regarded as the correct lead age. Independent support that the Rhodesian and Manitoban pegmatites are at least of a very similar age comes from strontium measurements (AHRENS and MACGREGOR, 1951; NICOLAYSEN *et al.*, 1953; NICOLAYSEN, 1954; DAVIS and ALDRICH, 1953; and SCHREINER *et al.*, 1955).

We will now examine the nature of the relationship between $t(\frac{207}{235})$ and $t(\frac{206}{238})$ in Fig. 1. Examination is facilitated if data can be transformed so as to yield a

linear relationship; this may be achieved by relating log $t(\frac{206}{238})$ to $t(\frac{207}{235})$ as in Fig. 2. The close fit of points emphasizes the close relationship between $t(\frac{207}{235})$ and $t(\frac{206}{238})$, and shows also that Manitoban monazite with its qualitatively distinct $t(\frac{206}{238}) > t(\frac{207}{235}) > t(\frac{207}{206})$ age distribution is slightly but distinctly displaced from an extrapolation through the convergent point $(t(\frac{207}{235}) = t(\frac{206}{238}) = t(\frac{207}{206}))$. The linear relationship is expressed by an equation of the type,

$$\log t(\tfrac{206}{238}) = at\,(\tfrac{207}{235}) + b \qquad (1)$$

where t = age in years and a the slope constant $= 3{\cdot}36 \times 10^{-10}$ and $b = 8{\cdot}525$.

A test of equation (1) is shown in Table 1, which compares measured $t(\frac{207}{235})$ with a value obtained from equation (1), using measured $t(\frac{206}{238})$ and the constants as given.

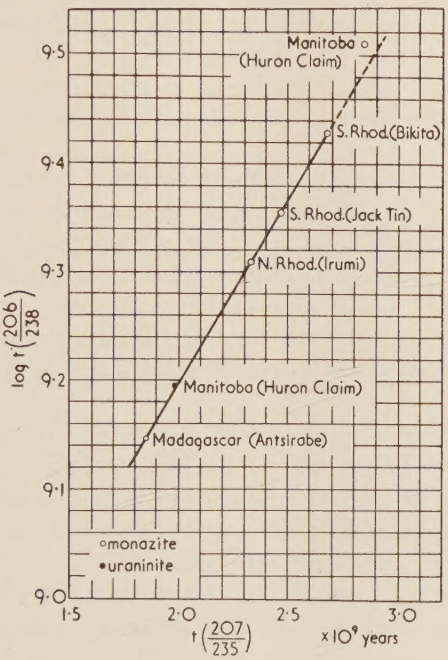

Fig. 2. Log $t(\frac{206}{238})$ appears to be linearly related to $t(\frac{207}{235})$ in all participants of the Rhodesia age pattern, with the exception of Manitoban monazite.

It is reasonable to anticipate that Rhodesia-type age patterns should exist at all ages. Although there is complete lead information on many individual specimens, only one other suite of specimens is currently available for examination. Age data on some fifteen uraninite and thucholite specimens coming mainly from sediments from different horizons within the gold producing Witwatersrand System of South Africa have recently been reported by Louw (1955). This valuable set of data on so many specimens is unfortunately not easily amenable to precision age calculation and comparison, mainly because the proportion of non-radiogenic lead is often quite high (a point stressed by Louw), and because the presence of two distinct types of uraninite has been observed (Liebenberg, 1948; Davidson and

Bowie, 1951). The presence of two generations of uraninite would not introduce serious difficulty provided their ages were similar, but Davidson (1955) reports a chemical age of only 160×10^6 years for a carefully separated uraninite from West Rand Consolidated; the estimated age of the specimen as a whole was more

Table 1. *Comparison of measured and calculated* $t(\frac{207}{235})$

	($\times 10^6$ *years*)	
	Measured	*Calculated*
Ebonite	2680	2680
Jack Tin	2470	2465
Irumi	2330	2330
Huron Claim (uraninite)	1985	1990
Antsirabe	1850	1850

(For details and references to original data, see Ahrens, 1955a).

than $\times 10$ this age. Louw, however, was able to conclude that because of a "high degree of correspondence" among the ages of various specimens, the effect of varying admixture did not appear as serious as may have been expected. Perhaps the proportion of primary or older uraninite is usually much greater than that of the secondary or younger generation uraninite. Although somewhat different ages have been recommended for individual specimens by Louw (1955) and Davidson (1955), both agree on a general magnitude of about 2000×10^6 years for most specimens.

No exhaustive discussion of the ages of individual Witwatersrand uraninite specimens or their mode of origin will be attempted here, as the emphasis is on general relationships, and although the relationships which we find may be altered somewhat in detail by changing the assumed constitution of non-radiogenic lead, they should nevertheless retain their main features.

Fig. 3 relates $t(\frac{207}{235})$ to $t(\frac{207}{206})$ and $t(\frac{206}{238})$. All data have been plotted with the exception of the Dominion Reefs* uraninite, which appears to be distinctly older than the other specimens. Specimens from the Black Reef and the Contact Reef are included because, although the reefs themselves are younger than the Witwatersrand system, the uraninites and thucholites which they contain may be of the same general age as those from the Witwatersrand System proper: this would hold regardless of whether a detrital or hydrothermal origin is postulated for the majority of the uraninites. In general there is a rough tendency to form a convergent-divergent age pattern of the Rhodesia type. For specimens U-2(a),* U-2(b), U-3, U-4, U-6, C-3, and C-4, the relationship between $t(\frac{207}{235})$ and $t(\frac{206}{238})$ seems close. The corresponding relationship between $t(\frac{207}{235})$ and $t(\frac{207}{206})$ is poor, and may be due to the sensitivity of $t(\frac{207}{206})$ to mass spectrometric error. Fig. 4 shows that the semi-logarithmic relationship (cf. Fig. 2 and equation (1)) appears to hold for

* For locality details including position of specimen in stratigraphic section see Louw (1955). U* = uraninite, C = thucholite.

specimens U-2(a), etc., of the Witwatersrand group. The greater slope for specimens of the Witwatersrand group as compared with that of the line for specimens of the Rhodesia group, which is given again for comparison, is due evidently to a

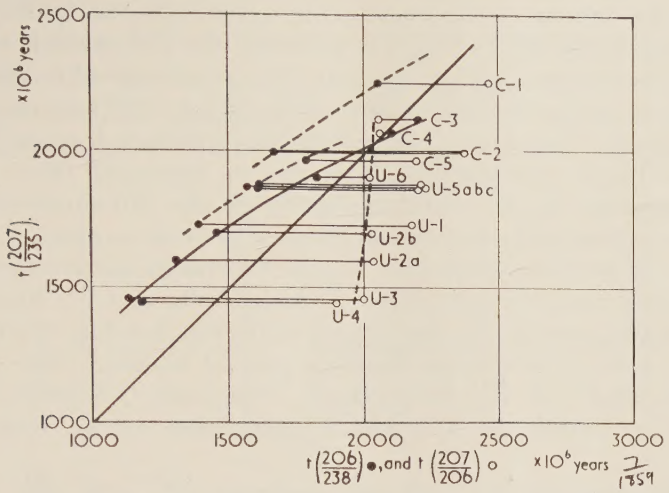

Fig. 3. Witwatersrand age distributions. The solid line curve indicates a fairly well developed regularity. Some other possible regularities are indicated by dashed lines.

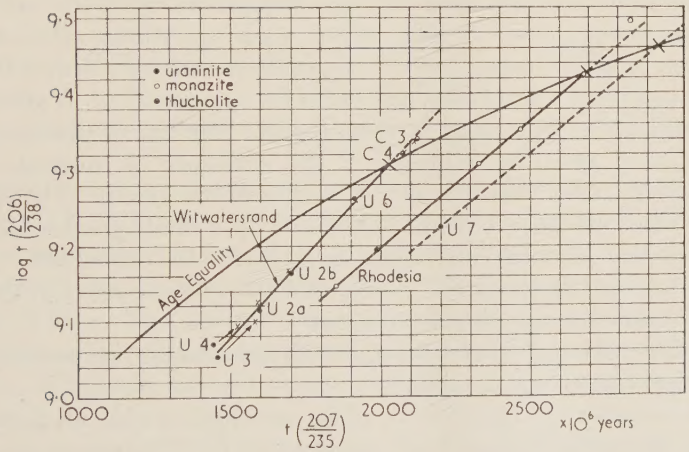

Fig. 4. The semi-logarithmic linear relationship for Witwatersrand and Rhodesia specimens. Two sets of Witwatersrand points are shown; those given by Louw, 1955 (circles) and those recalculated (x) on the basis of a lead isotope constitution of $Pb^{206} = 15{\cdot}5$ and $Pb^{207} = 15{\cdot}5$. Specimen U-7 is used as an example to illustrate a convergent age estimate based on one specimen only.

higher proportion of U^{238} in the Witwatersrand specimens; these are about one half-life of U^{235} younger (see below) than members of the Rhodesia group.

Unlike the Rhodesia example, no Witwatersrand specimen is located precisely

at the point of convergence (age equality); moreover, as the $t(\frac{207}{235})$ vs. $t(\frac{207}{206})$ relationship is poorly developed, a convergent age cannot be estimated merely by extrapolating the $t(\frac{207}{235})$ vs. $t(\frac{206}{238})$ and $t(\frac{207}{235})$ vs. $t(\frac{207}{206})$ curves until they meet. A satisfactory convergent age estimate involving $\frac{207}{235}$ and $\frac{206}{238}$ ages only may apparently be made by means of the linear semi-logarithmic relationships. Thus in Fig. 4 the convergent age $t(\frac{207}{235}) = t(\frac{206}{238})$ is given by the intersection of the extrapolation with a curve drawn for age equality. A similar type of estimate could be made in Fig. 3, by noting the intersection of the $t(\frac{207}{235})$ vs. $t(\frac{206}{238})$ curve with the line drawn for age equality, but a far more satisfactory estimate is made by using the linear semi-logarithmic relationship. The age so indicated (Fig. 4) for each participating specimen of the main regularity of the Witwatersrand group is 2040×10^6 years. Stratigraphic considerations give some support to the conclusion of age equality for these specimens. In the first place, each component of two groups of specimens from the same mine (U-2(a), U-2(b) and C-3 from Marievale; U-6 and C-4 from Blijvooruitzicht) participate in the relationship. Furthermore, all specimens come more or less from the same general horizon; that is, a section covered by Main, Bird, and Kimberley Reefs. Specimen U-5 (Main Reef) seems to be a distinct exception, as it is not a participant of the main regularity (Fig. 3).

The available evidence has indicated that $\log t(\frac{206}{238})$ and $t(\frac{207}{235})$ are linearly related for specimens of given age, and, if this is assumed to hold generally, it becomes possible to determine t(convergent) even if one or two specimens only have been analyzed. For two specimens, t(convergent) should be given by the intersection of an extrapolation of a line through the points with the curve for age equality. For a single specimen, the slope of the semi-logarithmic relationship must of course be known, in which case a line of correct slope is merely drawn through the point, and continued until it intersects the curve for age equality. A specimen from Klerksdorp, Transvaal (Louw, 1955), is an example. The age of this specimen is of unusual interest, as it provides evidence of the existence of minerals which are slightly but distinctly older than the Rhodesia-Manitoba group. The slope of the intersecting line is not precisely known, but should be a shade greater than that for the Rhodesia specimens, and the convergent age is estimated at $\sim 2930 \times 10^6$ years. This estimate is regarded as tentative, partly because of the nature of the material and because it is based on one observation only.

The relationship between slope and age will presumably be worked out once further sets of observations are available.

We may now consider the significance of an assumption that all published lead age distributions are participants of age patterns of the Rhodesia type. Although confirmatory evidence is desirable, the assumption does have considerable backing. In the first place, if we accept the Rhodesia age pattern as a properly established fact, there seems to be no reason why totally different age patterns, brought about by different causes, should come into existence at other ages. The Witwatersrand example, though not a particularly good one, is supporting evidence. Age patterns at younger ages should be quantitatively distinct, because younger specimens will have inherited higher proportions of U^{238}, but they should be of the same general type. Secondly, the Rhodesia age pattern resembles the distribution of all published

ages when considered as a whole (Fig. 5). In each, the distribution $t(\frac{207}{206}) > t(\frac{207}{235}) > t(\frac{206}{238})$ is by far the most common, amounting to some three-quarters or so, and discordance varies enormously; a much smaller proportion have $t(\frac{206}{238}) > t(\frac{207}{235}) > t(\frac{207}{206})$ and age equality distributions.

Validity of Lead Ages in General and the Lead Age Scale as a Whole

The majority distributions $(t(\frac{207}{206}) > t(\frac{207}{235}) > t(\frac{206}{238}))$ will be discussed first. Consider again the Rhodesia pattern; with the exception of Ebonite ages all individual ages are underestimates, at least to some extent. $\frac{207}{206}$ ages are by far the

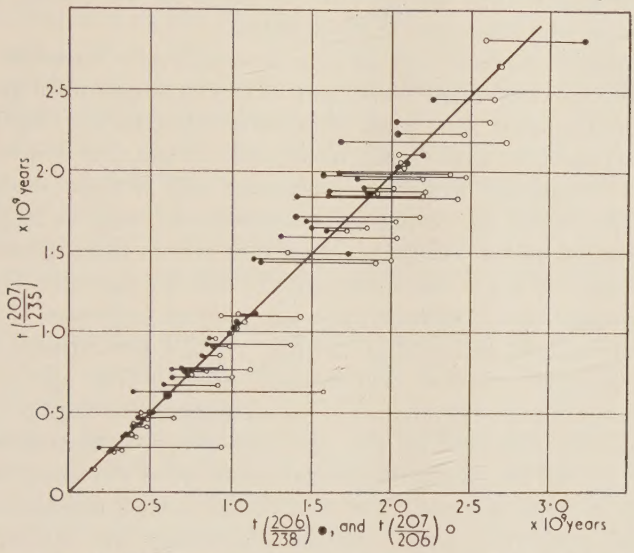

Fig. 5. Lead age distributions (uranium isotopes only). Data mainly from Faul (1954) and Louw (1955).

closest to the convergent age, and even in the Antsirabe specimen, an extreme example, $t(\frac{207}{206})$ is only ten per cent less than the convergent age. All other individual ages are more or less serious underestimates, in the order $t(\frac{207}{235}) > t(\frac{206}{238}) > t(\frac{208}{232})$; the $\frac{208}{232}$ age of the Antsirabe specimen is barely one-quarter of its convergent age and is about the most extreme example of its kind. It will be assumed that the above observations about the individual estimates of the ages of participants of the Rhodesia pattern apply generally to specimens having $t(\frac{207}{206}) > t(\frac{207}{235}) > t(\frac{206}{238})$.

The conclusion that $t(\frac{207}{206})$ is the most reliable single estimate accords with the recommendation of Nier (1939), Nier *et al.* (1941) and Collins *et al.* (1954), and is based partly on the fact that recent gain or loss of either lead or uranium does not influence this ratio. It is generally agreed, however, that $\frac{207}{206}$ estimates tend to be unreliable at young ages, because $t(\frac{207}{206})$ becomes less time-sensitive and is prone to serious error arising from uncertainty of a common lead correction. In their summing up of the present status of the lead method, Kulp *et al.* (1954) conclude that $t(\frac{207}{235})$ is generally the most reliable single estimate. This conclusion is based in part on the assumption of significant radon escape from specimens with $t(\frac{207}{206})$

$> t(\frac{207}{235}) > t(\frac{206}{238})$; this would depress $t(\frac{206}{238})$ and elevate $t(\frac{207}{206})$, but not influence $t(\frac{207}{235})$. The above interpretation of the Rhodesia age pattern is strong evidence against the recommendation of the general use of $t(\frac{207}{235})$ as a valid estimate.*

Use may also be made of the ratio Pb^{206}/Pb^{210} as an estimate of age (HOUTERMANS, 1951; BEGEMANN *et al.*, 1953; and KULP *et al.*, 1953). The number of published ages is still small, but they indicate that $t(\frac{206}{210})$ is often similar to $t(\frac{206}{238})$. If so, $\frac{206}{210}$ ages will usually be serious underestimates; further observations on suites of specimens of given age are required, however, before firm conclusion can be made. We should note that in a private communication to KOHMAN and SAITO (1954), KULP states that the $\frac{206}{210}$ ages of KULP *et al.* (1953) require some revision, as a result of re-calibration of equipment.

We may now turn to the lead age scale as a whole, as a measure of geological time. From time to time, attempts have been made to construct a geological time scale based on recommended lead ages of selected specimens. Earlier attempts (HOLMES, 1937, for example) were based on chemical ages, but recently (HOLMES, 1948, for example) completely analyzed (chemical and isotope analysis) samples have been used. The actual age which is recommended may be $t(\frac{207}{206})$ or perhaps $t(\frac{207}{235})$, based on assumed radon escape; sometimes it has been possible to use a specimen with concordant ages. An assumption that the age distribution of each specimen is a participant of a Rhodesia type age pattern indicates that the recommended ages of specimens with $t(\frac{207}{206}) > t(\frac{207}{235}) > t(\frac{206}{238})$ are underestimates; the magnitude of the required increase will depend upon which age ($t(\frac{207}{206})$, $t(\frac{207}{235})$, or other) was recommended in the first place, and second on the degree of the internal disagreement as may be indicated by Fig. 1. With the exception of the Rhodesia-Manitoba example, it will be impossible to calculate what revisions are predicted; we may say, however, that the net effect will be an overall expansion of the lead scale for measuring geological time. Before discussing the Manitoba-Rhodesia example in detail we will consider briefly the age of the upper Cambrian kolm from Gullhögen, Sweden. Although not mineralogically satisfactory, this specimen has nevertheless been one of the very few dated specimens whose relative geological age (upper Cambrian) is accurately known from the fossil record. Individual age estimates are, $t(\frac{207}{206})$ (800×10^6 years), $t(\frac{207}{235})$ (440×10^6 years) and $t(\frac{206}{238})$ (380×10^6 years). On the basis of assumed radon escape (WICKMAN, 1942), $t(\frac{207}{235})$ has been recommended for the upper Cambrian, but if we assume that the age distribution of the kolm specimen is a participant of a convergent age pattern, a magnitude of slightly greater than 800×10^6 years must be considered as a possible magnitude of the upper Cambrian.

The Rhodesia-Manitoba example is particularly satisfactory, as pegmatites from these areas are among the oldest of all thus far investigated (AHRENS, 1955b, with reference to earlier papers); consequently their age is regarded as very early pre-Cambrian, and has served as a lower limit for constructing a geological time

* *Footnote added in proof.* ECKELMANN and KULP (in press) have examined the lead ages of a suite of *pitchblende* specimens from the Lake Athabasca area and conclude (i) that Pb loss and not Rn loss (compare earlier discussions by KULP and co-workers) is the principal cause of internal disagreement, (ii) that individual age estimates of their samples are underestimates, and (iii) that $t(\frac{206}{210})$ agrees with $t(\frac{206}{238})$. Conclusions (i) and (ii) are very similar to some of those arrived at in this paper.

scale. In his first attempt, HOLMES (1937) used the chemical age of 1700×10^6 years for Manitoba uraninite as the lower limit of his geological time scale. The appearance of complete isotope information led to an increase of the recommended age to 1985×10^6 years (HOLMES, 1948). This age was based on assumed loss of 31·4 per cent radon. The fact, however, that the $\frac{207}{206}$ age (2475×10^6 years) of this specimen is close in magnitude to the $\frac{207}{206}$ age (2590×10^6 years) of monazite from the same locality, has led COLLINS *et al.* (1954), following NIER *et al.* (1941), to recommend a magnitude of 2500×10^6 years, rather than one of 2000×10^6 years; this recommendation has since been accepted by HOLMES (1954). It seems, however, that even this estimate is low, and that the convergent age of 2680×10^6 years for participants of the Rhodesia pattern is the most likely one. This overall increase in age (1700 to 2680×10^6 years) amounts to about 1000×10^6 years.

Modern strontium age determinations tend to be systematically greater than previously recommended lead ages, and a strontium age scale would be considerably longer than any of the previously constructed lead age scales. It has been customary in the past to consider the lead age scale as the closest approach to a true geological time scale, and to regard a possible strontium age scale as seriously aberrant. An assumption, however, that convergent lead ages are the most accurate lead estimates would bring the lead age scale much closer into line with a strontium age scale.

The possible significance of minority distributions ($t(\frac{206}{238}) > t(\frac{207}{235}) > t(\frac{207}{206})$) has thus far not been considered; about one in five to ten of the published distributions are of this type. Whether they are true participants of age patterns or not seems to depend on whether all age distributions have the same cause, but in varying degree. It will be recalled that the decay constant of U^{235} is apparently not known with the same accuracy as that of U^{238}, and that an increase of say a few percent would bring about convergence in the Rhodesia pattern at about 3000×10^6 years—that is, at an age close to the $\frac{206}{238}$ age of the Manitoban monazite. The Manitoban monazite distribution is, however, distinctly displaced (cf. also C-3 and C-4 in the Witwatersrand pattern) and a different cause for such distributions is indicated (see discussion below). Though decidedly scant, this evidence is against true participation of the $t(\frac{206}{238}) > t(\frac{207}{235}) > t(\frac{207}{206})$ distributions in age patterns, and the tentative conclusion is made that the present convergent point remains the closest estimate of the correct age. Its precise location is, however, still open to some uncertainty, and must await further detailed investigation on suites of specimens, some having the minority age distribution. Meanwhile we should note that strontium (isotope-dilution procedure) ages (DAVIS and ALDRICH, 1953; NOCOLAYSEN *et al.*, 1953; NICOLAYSEN, 1954; SCHREINER *et al.*, 1955) support the $\frac{206}{238}$ magnitude of the Manitoban monazite as the correct age of the Rhodesia-Manitoba specimens, whereas argon measurements (WILSON *et al.*, 1954) support a lower age.

A Note on Chemical Lead Ages

Chemical $\left(\frac{\text{total Pb}}{\text{U} + \text{Th}}\right)$ estimates were often regarded as overestimates, as no allowance could be made for possible presence of a significant proportion of non-radiogenic lead. Age data on participants of the Rhodesia pattern (Table 1) indicate

quite definitely that, in these specimens at least, all chemical ages are serious underestimates, with the exception of the Ebonite specimen; in the Antsirabe specimen, the chemical age is only about one-quarter of t(convergent).

Table 2. Chemical ages of participating specimens of the Rhodesia age pattern. (The correct Pb *age of each specimen is regarded as* 2680×10^6 *years)*

Specimen	*Chemical age* ($\times 10^6$ *years*)
Monazite; Ebonite (Rhod.)	2680
Monazite; Jack Tin (Rhod.)	2020
Monazite; Huron Claim (Man.)	1955
Uraninite; Huron Claim (Man.)	1680
Monazite; Irumi (Rhod.)	1500
Monazite; Antsirabe (Mad.)	700

For locality details, see references to various papers (Holmes and others) given by Ahrens (1955a).

This leads to a generalization that the majority of all crude ages are underestimates. (In highly active minerals, this conclusion is not likely to be influenced by the presence of common lead, as its proportion is usually insignificant.) This conclusion is not of much significance when complete information is available, because chemical ages would not then be used; but when rapid chemical ages are carried out purely for the sake of reconnaissance, the possibility of obtaining a serious underestimate should be remembered. It will be recalled also, that a vigorous attempt is now being made to develop a rapid method (Larsen *et al.*, 1952; see also Faul, 1954) applicable to certain accessories (zircon, titanite, apatite, and others) in igneous rocks. The ratio of total Pb to total activity is measured as a function of age. Although it is understood that such estimates are not intended as precision ages, the possibility that some such ages may be serious underestimates, at least in the pre-Cambrian, should not be overlooked. In making this statement, we assume that the proportion of non-radiogenic lead is insignificant. It may, of course, be argued that the conclusion of the tendency of chemical ages to be underestimates is based on observations on monazites and uraninites, and that therefore this does not apply to zircon, etc. Adequate data are unfortunately not available, but the few complete ages show the common $t(^{207}_{206}) > t(^{207}_{235}) > t(^{206}_{238}) > t(^{208}_{232})$ age distribution (see for example, zircon from Cape granite —Table 9 of Faul, 1954), and the data as interpreted here show that a chemical age would be an underestimate.

Causes of Lead Age Distribution

The principal conclusions (Ahrens, 1955a) about a possible cause of the Rhodesia age pattern have been noted above in the introduction. Before proceeding further it will be necessary to point out that the term "lead loss" was misused in the previous paper as a general term, and that lead deficiency has been substituted in the

present paper; apparent lead deficiency could be produced by loss of lead itself, escape of an intermediate member of a decay chain, or perhaps by some other process. We will consider the majority distribution ($t(^{207}_{206}) > t(^{207}_{235}) > t(^{206}_{238})$) first. The high degree of order in Fig. 1 has been taken as evidence favouring physical control of lead deficiency rather than a chemical leaching of lead. Further evidence against recent chemical loss of lead is seen in Fig. 6. The calculated (dashed line)

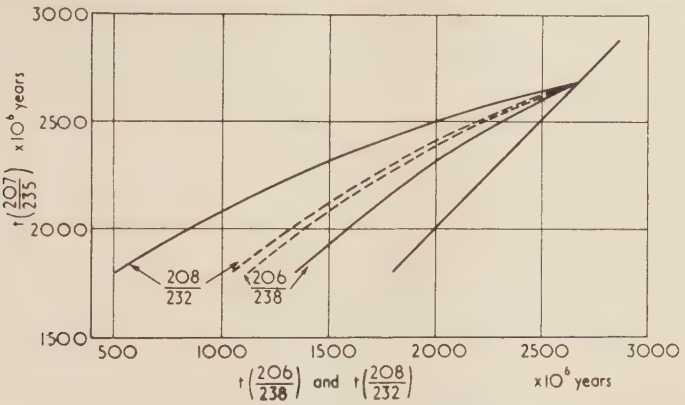

Fig. 6. A comparison of observed age curves (solid line) with those based on assumed recent loss of varying proportions of lead from Rhodesian (Ebonite) monazite (dashed line). The straight line of unit slope is for age equality.

curves based on assumed recent loss of varying proportions of lead indicate that, although ages would be depressed in the order $t(^{208}_{232}) > t(^{207}_{235}) > t(^{206}_{238})$, they are quite distinct from those based on observation, and this, taken together with the fact that $t(^{207}_{206})$ would have remained unaffected by recent lead loss, is strong evidence against this possibility. The same reasoning rules out the possibility that incomplete precipitation of lead during chemical analysis could have been the cause of the Rhodesia age pattern, and of $t(^{207}_{206}) > t(^{207}_{235}) > t(^{206}_{238})$ distributions in general.

The semi-logarithmic relationship (equation (2)) should serve as a guide when seeking the actual mechanism which has brought about apparent lead deficiency. The age vs. age relationship involves relating

$$\frac{2{\cdot}303}{\lambda_U 235}\log_{10}\left(1+\frac{N_{207}}{N_{235}}\right) \text{ to } \frac{2{\cdot}303}{\lambda_U 238}\log_{10}\left(1+\frac{N_{206}}{N_{238}}\right)$$

and although undoubtedly of use in this form, it would be more instructive to consider the last term only (ratio of daughter atoms to parent atoms) of the age equation. Atomic ratios (Rhodesia group only) are given in Table 3, and Fig. 7 relates $\frac{N_{207}}{N_{235}}$ to $\frac{N_{206}}{N_{238}}$ for specimens of the Rhodesia and Witwatersrand (only U-2(a), (b), etc.) groups.

The total number of observations is not large, but they are nevertheless able to indicate strongly that the relationships are not exponential but linear, or at least very nearly so. For participants of the Rhodesia pattern, the relationship between the two variables is,

$$\frac{N_{207}}{N_{235}} = a\frac{N_{206}}{N_{238}} - b \qquad (3)$$

Table 3. Pb-U *isotope ratios for participants of the Rhodesia age pattern*

	$\frac{N_{206}}{N_{238}}$	$\frac{N_{207}}{N_{235}}$	$\frac{N_{208}}{N_{232}}$
Monazite (Manitoba)	0·634	14·75	
Monazite (Ebonite)	0·507	12·45	0·143
Monazite (Jack Tin)	0·42	10·1	0·1013
Monazite (Irumi)	0·383	9·02	0·0714
Uraninite (Manitoba)	0·27	5·85	
Monazite (Antsirabe)	0·241	5·16	0·0299

($a = 27{\cdot}7$ and $b = 1{\cdot}6$). A similar expression seems to hold for the Witwatersrand specimens. Fig. 8 relates $\frac{N_{207}}{N_{235}}$ to $\frac{N_{208}}{N_{232}}$ for four participants (monazites only) of the Rhodesia pattern; a linear relationship again seems to hold, namely

$$\frac{N_{207}}{N_{235}} = a\frac{N_{208}}{N_{232}} + b \qquad (4)$$

($a = \sim 64$ and $b = \sim 3{\cdot}4$).

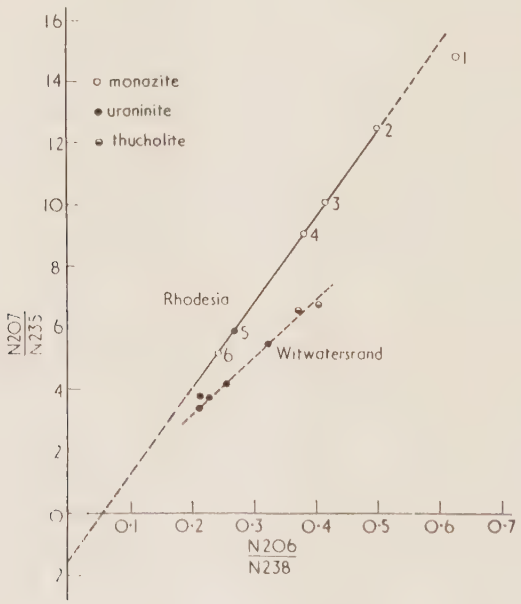

Fig. 7. The relationship between U-Pb isotope ratios for participants of the Rhodesia pattern and for some (U-2(a), etc.) Witwatersrand specimens. Numbering of Rhodesia group as in Fig. 1, and order of points of Witwatersrand group as in Fig. 4.

The sign of the constants a and b in equations (3) and (4) indicates that deficiency of 208 is greatest, but that for the uranium leads, 207 is more deficient than 206. This

cannot be recognized from the curves (Fig. 1), and the $t(^{207}_{206}) > t(^{207}_{235}) > t(^{206}_{238})$ distribution in general indicates that deficiency of 206 should be greater than 207, as $t(^{207}_{235})$. On this basis also AHRENS (1955a) had mistakenly assumed a deficiency of 206 greater than 207. The cause of this reversal of order is due to the age equation itself, and to the fact that the half-life of U^{235} is much less than that of U^{238}, and unless deficiency of 207 is much greater than 206, $t(^{207}_{235})$ will be greater than $t(^{206}_{238})$. This may be illustrated further by means of Fig. 6, which has served to compare the observed age curves with those calculated on the basis of recent loss of varying proportions of lead. Under such conditions, equal proportions of 206

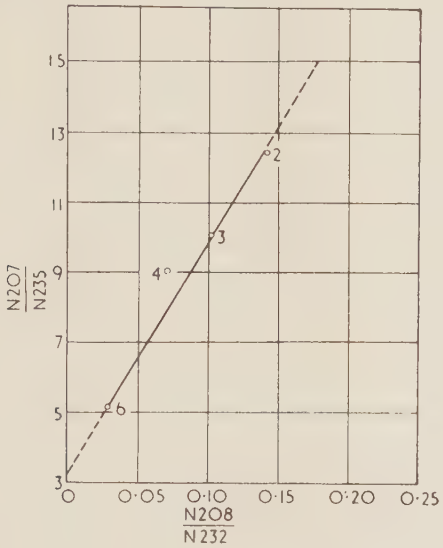

Fig. 8. The relationship between $\frac{N_{207}}{N_{235}}$ and $\frac{N_{208}}{N_{232}}$ in four specimens of monazite. Numbering as in Fig. 1.

and 207 would be lost, but $t(^{206}_{238})$ is lowered much more than $t(^{207}_{235})$. As a specific calculation may be helpful, consider the specimen of Ebonite monazite (Fig. 1), whose age has been estimated at 2680×10^6 years. A recent loss of say three-quarters of its lead would reduce $t(^{208}_{232})$ to almost exactly one-quarter of 2680×10^6 years, because the half-life of Th^{232} ($1{\cdot}39 \times 10^{10}$ years) is considerably greater ($\sim \times 5$) than the age of the mineral, and hence the relationship between lead loss and age is linear. For $t(^{206}_{238})$, the age would decrease to slightly greater than one-quarter of the convergent age, as the half-life of U^{238} ($4{\cdot}5 \times 10^9$ years) is moderately greater ($\sim \times 1{\cdot}7$) than t(convergent). The half-life of U^{235} ($7{\cdot}1 \times 10^8$ years) is, however, only one-quarter of t(convergent), and a loss of three-quarters of 207 reduces $t(^{207}_{235})$ by only one-half; that is, to an age roughly double that of $t(^{208}_{232})$ and $t(^{206}_{238})$. In Fig. 6 the curve based on observation is displaced toward the line for age equality, because deficiency of 207 is proportionately greater than 206; a far higher proportionate deficiency of 207 is required, however, before this curve would move across that for age equality. It should be emphasized that the ratio $\frac{207}{206}$ (Table 1 of AHRENS, 1955a) and hence $t(^{207}_{206})$, decreases with apparent increases of lead deficiency (Fig. 1), and this could only happen provided deficiency of 207 were

greater than that of 206. For $^{208}_{232}$, the curve for observed $t(^{208}_{232})$ is displaced from that based on calculation in a direction away from the line of age equality, because deficiency of 208 is greater than 207 (equation (4)).

Differential loss of emanation is a possible physical process causing varying lead isotope deficiency, in which case the deficiency order of 208 > 207 > 206 might be expected to vary either with half-life of emanation or of recoil energy of the intermediate parent, as indicated by the respective α-particle energies. Neither of these properties indicates a deficiency order as observed. Measurements reported by Kulp *et al.* (1954), Giletti and Kulp (1955), and Davidson (1955) indicate that emanation escape from uraninites and presumably monazites is too low to account for the magnitude of lead deficiency often found. Before closing the discussion on the cause of the $t(^{207}_{206}) > t(^{207}_{235}) > t(^{206}_{238})$ distribution, we should note (i) that uraninite, often a metamict mineral, appears to be a true participant of the Rhodesia age pattern, the structure of which has been established by the age distribution of monazites (never metamict, and with different structure), and (ii) that the Witwatersrand regularities, which are of a very similar type, have been determined mainly by uraninite, and also in part by thucholite, a carbonaceous material. One wonders then whether an escape process operating in such distinctly different minerals would bring about such close relationships, and this opens up a possibility (Mayne, 1955) that some other not properly understood nuclear process could conceivably be the cause.

Nier *et al.* (1941) and others, mainly Holmes (several papers), point out that uranium loss would elevate all ages, in the order $t(^{206}_{238}) > t(^{207}_{235}) > t(^{207}_{206})$, and such a cause is usually suggested for age distributions of this type. The $^{207}_{206}$ age would not be affected if such loss took place recently. Consider now the Manitoban monazite (Fig. 1). The age distribution is $t(^{206}_{238}) > t(^{207}_{235}) > t(^{207}_{206})$. Uranium loss has been suggested (Holmes, 1948), and support may be found in the fact that the $^{207}_{235}$ and $^{206}_{238}$ ages appear elevated; that is, greater than the convergent age of 2680×10^6 years. The same general comments apply to specimens C-3 and C-4 in the Witwatersrand age pattern. The convergent point can, of course, be manipulated by changing the half-life of U^{235}, as already noted, but such manipulation cannot bring about precise fit of the Manitoban monazite age distribution on the Rhodesia pattern. Moreover, the $^{207}_{206}$ value of 0·1705 for the Manitoban monazite is actually less than the value (0·181) for the convergent point (Ebonite specimen); the same general comments apply to specimens C-3 and C-4 of the principal Witwatersrand regularity. Though scant, this evidence may be regarded as against the possibility that the $t(^{206}_{238}) > t(^{207}_{235}) > t(^{206}_{207})$ distribution has been caused solely by the same mechanism which, operating in varying degree, has caused the majority distribution; if such had taken place, perfect fit would be anticipated. A plausible but purely tentative suggestion is, therefore, that specimens with $t^{206}_{238} > t(^{207}_{235}) > t(^{207}_{206})$ have recently lost uranium, but that such loss has taken place from specimens in which the mechanism which causes apparent lead deficiency has in any case operated to some degree ($^{207}_{206}$ evidence). It seems quite clear that full-scale investigations, involving Pb^{206}/Pb^{210} and emanation measurements as well, on several suites of specimens at various ages, are most urgently required for the purpose of guiding us to a satisfactory solution to the problem of the actual cause(s) of the lead age distributions.

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The argon-40 content of the atmosphere and the age of the earth

H. A. Shillibeer and R. D. Russell
University of Toronto

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ABSTRACT

Applying the theory that the continents have been formed by the addition of volcanic material from depth during geologic time, and assuming that this material released all of its radiogenic argon-40 while it was in the molten state, an age of the earth has been calculated from the argon-40 content of the earth's atmosphere. Using current estimates of the potassium content of the crustal rocks, volume of the continents, and the argon-40 content of the atmosphere, we find that all the argon-40 in the atmosphere could have been released in this way if the earth were 5,300 million years old. This value is in reasonable agreement with other estimates of the age of the earth and of the universe. It is therefore concluded that this is a reasonable explanation for the derivation of the earth's atmospheric argon.

Introduction

The abundances of the inert gases on the earth are very low compared with estimated cosmic abundances. The amount by which these gases have been depleted can be approximately correlated with their atomic weights, with the exception of argon-40, which is over one hundred times too abundant (Brown, 1949). This has led to the acceptance of von Weizächer's theory (1937) that the argon-40 in the earth's atmosphere is radiogenic in origin, being produced by the decay of potassium-40. Owing to the high mass of argon-40, it is doubtful if a significant amount of argon has been lost from the atmosphere as a result of the atoms attaining escape velocity.

Several authors have recently published papers concerning this high proportion of argon-40 in the earth's atmosphere (Tatel, 1950; Birch, 1951; Kulp, 1951; and Rankama, 1953). The calculations of Tatel (1950) and Kulp (1951) indicated that there is far too much argon-40 in the atmosphere for it to have been derived from the potassium-40 contained in the crustal rocks alone. On the other hand, Rankama (1953) showed that all the argon-40 could have been derived by the weathering of a hypothetical 22-km layer of the crust in the past 3,500 million years. Birch (1951) also suggested that all the argon-40 could have been derived from the crustal rocks alone. In all cases the conclusions reached depend critically on the value taken for the earth's age. Tatel and Kulp assumed a meteoritic model for the earth's mantle, while Birch made calculations with both meteoritic and dunite models of the mantle.

Recent theories of the growth of continents provide a much more probable origin for the argon-40 in the atmosphere, by assuming its release as the continents are formed. We find that argon released with the formation of the earth's crust can by itself account for all the argon in the atmosphere. This paper demonstrates that this single assumption is sufficient to enable us to calculate a value for the age of the earth which agrees with other independent estimates.

Basis of Calculation

Age determinations made all over the world suggest that the continents have been continuously formed during geologic time. The results show that in all the continents so far investigated one or more nuclei exist. The ages of these nuclei are always greater than 2,000 million years, and they represent the oldest known rocks. These nuclei are surrounded by belts of rocks which are progressively younger at greater distances from each nucleus (Wilson, 1954). This has led to the suggestion that the continental blocks were formed by successive additions of volcanic material. Wilson (1952) has shown that the rate of production of lava and ash from existing volcanoes is sufficient to have produced all the material of the continents in geologic time. While this lava was in the molten state it is highly probable that it released to the atmosphere all the radiogenic argon-40 that it contained. The present calculations are based on this assumption.

The structure of the continental blocks appears to be fairly uniform down to the Mohorovičić discontinuity. It was originally considered that there were at least two different layers in the continental blocks, but more recent seismological evidence indicates that there is a change to higher-density rocks towards the base, but no definite boundary has been found. At the Mohorovičić discontinuity the velocity of the P waves changes abruptly from about 6 km/sec to nearly 8 km/sec.

The depths of the continental blocks was obtained by averaging six results obtained in various parts of the world for the position of this sudden change in the velocity of the P waves. The results are given in Table 1, which also gives the location of the measurements. The mean thickness of the continental blocks from these results is 36 km.

Table 1. *Depth of Mohorovičić discontinuity*

Location	North Germany	West Transvaal, Africa	Wisconsin, U.S.A.	Central Appalachian, U.S.A.	Central Atlantic Coastal Region, U.S.A.	Canadian Shield
Author and reference	Willmore (1949)	Willmore, Hales, and Gane (1952)	Slichter (1951)	Adams, Tuve, and Tatel (1951)		Hodgson (1953)
Total depth in kilometres	27·4	34·2	40–44	33	40–50	35

In addition we have assumed a 5-km thickness of basalt over the ocean floors. The depth and nature of this layer is substantiated by the seismological results of Ewing (1953), Hess (1954), Hill and Laughton (1954), and Gaskell (1954). We have assumed that the bottom 5 km of the continental blocks are basaltic, being a continuation of the basaltic layer under the oceans. This assumption is substantiated by the apparent increase in density found near the base of the continental blocks. The upper 31 km of the continents are assumed to have the average

potassium content and density of the exposed continental igneous rocks, and the remainder that of basalt. The above ideas of the structure of the crust down to the Mohorovičić discontinuity are essentially in agreement with those given by Hess (1954) and Bullard (1954).

Calculation of the Earth's Age

Using this model for the earth's crust, we can now calculate the time-interval required for the potassium-40 contained in these rocks to have formed all the argon-40 in the atmosphere.

By using the following data we can calculate the mass of potassium-40 contained in the crustal rocks:—

Density of exposed continental rocks	—	2·7 g/cc (Gutenberg, 1951a)
Density of basalt	—	2·9 g/cc (Gutenberg, 1951a)
Area of land	—	$1{\cdot}49 \times 10^{18}$ cm^2 (Gutenberg, 1951b)
Total surface area of earth	—	$5{\cdot}1 \times 10^{18}$ cm^2 (Gutenberg, 1951b)
Percent potassium in continental rocks	—	2·6 (Rankama and Sahama, 1950a)
Percent potassium in basalt	—	1·26 (Rankama and Sahama, 1950b)
Percent potassium-40 in potassium	—	0·0119 (Nier, 1950)
Therefore the mass of basaltic rocks	—	$5{\cdot}1 \times 10^{18} \times 5 \times 10^{5} \times 2{\cdot}9 = 7{\cdot}395 \times 10^{24}$ grams
Therefore the potassium-40 content of the basaltic rocks	—	$7{\cdot}395 \times 10^{24} \times 0.000119 \times 1{\cdot}26 \times 10^{-2} = 1{\cdot}109 \times 10^{19}$ grams
Similarly the potassium-40 content of the continental blocks down to 31 km	—	$= 3{\cdot}858 \times 10^{19}$ grams
Therefore the present mass of potassium-40 in all continental rocks and the ocean floor above the Mohorovičić discontinuity	—	$= 4{\cdot}967 \times 10^{19}$ grams

The following equation for the mass of argon-40 that has been produced between the time t_0 and t by the radioactive decay of potassium-40 is

$$A^{40} = K^{40} \cdot \frac{R}{1+R} \{e^{\lambda t_0} - e^{\lambda t}\} \qquad (A)$$

The factor $R/(1 + R)$ denotes the proportion of potassium-40 atoms decaying to form argon-40, where R is known as the branching ratio of potassium-40; a value of 0·089 has been used for this ratio (Shillibeer, Russell, Farquhar, and Jones, 1954). For λ, the total decay-constant of potassium-40, a value of $0{\cdot}55 \times 10^{-9}$ has been used (Shillibeer and Russell, 1954).

In this equation t_0 is the age of the earth and t is the average age of the crustal rocks. We have taken $t = 1{,}500$ m.y. If all the crustal rocks had continually lost all their argon, which seems to us untenable on the basis of potassium-argon age studies, then $t = 0$, and t_0 would be lowered by only 4 per cent. We have assumed that all the argon was released by the crustal rocks at the time of their emplacement. If this were not true, potassium-argon ages for rocks should be anomalously high: this has never been observed. If it is assumed that the basalt does not extend

beneath the continents, the value obtained for the age of the earth would be lowered by only 2 per cent.

The total argon content of the atmosphere is $6{\cdot}55 \times 10^{19}$ grams (Rankama and Sahama, 1950c), and since argon-40 forms 99·6 per cent (Nier, 1950) of all the argon, the atmosphere contains $6{\cdot}52 \times 10^{19}$ grams of argon-40. Assuming that all this has been formed by the radioactive decay of potassium-40, we have from the equation:

$$6{\cdot}52 \times 10^{19} = 4{\cdot}967 \times 10^{19} \cdot \frac{0{\cdot}089}{1{\cdot}089} \{e^{\lambda t_0} - e^{\lambda t}\}$$

$$\therefore \qquad e^{\lambda t_0} = 16{\cdot}06 + e^{\lambda t}$$

Assuming that the average age of the crust is 1,500 million years,

$$t_0 = \frac{10^9}{0{\cdot}55} \ln \{18{\cdot}34\} = \frac{2{\cdot}91}{0{\cdot}55} \times 10^9$$

$$= 5{,}300 \text{ million years.}$$

The value assumed for the average age of the crust can vary considerably and cause little change in t_0. This is shown by Table 2, which shows the variation in t_0 caused by different values of t.

Table 2

Value taken for t (millions of years)	*Value taken for t_0 (millions of years)*
0	5200
1000	5200
1500*	5300*
2000	5400
2500	5400

* Value preferred by the writers.

The age of the rocks near the Mohorovičić discontinuity, and especially the basaltic layer, must be as old or older than the exposed rocks, and consequently the above ages may be too small. On the other hand, the age could be lowered five hundred million years by using a branching ratio of 0·125, a value preferred by some writers.

Recent experiments by Boato, Careri, and Santagelo (1952) indicate that radiogenic argon-40 is being emitted by some active volcanoes. This supports our fundamental assumption that the earth's argon is a product of volcanic activity. However, if some volcanoes release radiogenic argon, without at the same time producing continental material, our age calculated for the earth would be too large. In addition to this, there is the possibility that at some time in the early history of the earth radiogenic argon escaped from a considerable depth due to melting of the mantle. The existence or exact nature of this melting is uncertain,

as is the potassium content of the mantle. Consequently it is impossible to say more than that any correction for such melting would lower our t_0.

Conclusion

It should be noted that calculations of the age of the earth based on variations in isotopic abundances of common leads determine the time at which the mantle of the earth could first maintain permanent heterogeneities in its uranium and lead contents (Russell and Allan, in press). The present calculation determines the time at which the earth contained essentially no argon-40. It is not evident that the latter age should be equal to the former.

Table 3 shows a comparison of various values of the "age of the earth" and the "age of the universe." It seems significant that our age of 5,300 m.y. based on the production of argon is in general agreement with the others. We therefore conclude that the bulk of the earth's argon can be explained by the release of radiogenic argon by crustal rocks as they are built into the continental masses.

Table 3. *Comparison of ages of the earth, stars, and meteorites*

	Method	*Age m.y.*	*Author*
Age of earth	Comparison of terrestrial and meteoritic leads	4500 ± 300	Houtermans (1953) Patterson *et al.* (1953)
	Variations in isotopic abundances of common leads	4200 ± 400	Russell and Allan (in press)
	Argon-40 content of atmosphere	5300	Present authors
Age of earth-moon system	Tidal friction theory	4000	Jeffreys (1952)
Age of stars	Expansion of universe	3500 < to < 7800	A. Sandage (1950)
	Expansion of universe	4900	W. Baade, reported by A. Sandage (1950)
	Theory of the evolution of stars	5100	A. Sandage (1953)
Age of meteorites	Potassium-argon ratio	4700 ± 200 4600 ± 200	Wasserburg and Hayden (1955)

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Metamorphism of natural waters in the crust of weathering — 1

I. I. Chebotarev
Australia

CONTENTS

Part 1

PAGE

Introduction 23
Scope of the problem 23
Sources of data and principles applied 24
General notes 24
Frequency curves 26
Ionic ratios 27
Acknowledgements 27
Theoretical Aspect 28
Previous concepts 28
Migration of soluble salts 29
Cycle of weathering 29
Mobility of soluble salts 31
Chemical relationship of rock to water 36
Geochemistry of subterranean waters 40
Motion of water 40
Geochemical classification of waters 41
Relationship of salt to fresh water 43
References 47

Part 2

Study of the Problem

Hydraulics and salinity of waters
Types of the artesian "systems"
Hydraulic gradients and salinity
Depth and salinity of water
Salinity with distance from the outcrop and from the sea
Depth and salinity of water in the Great Artesian Basin
Subterranean waters in oilfields
Substance of the problem
Method of grouping
Chemical composition of water
Hydraulic gradients and velocity of flow
Practical view
Chemical composition of natural brines
Oilfield brines
"Connate" brines
Change in salinity concentration of brines
Salt domes and associated waters
Subterranean waters of volcanic association
Waters of geysers
Waters of mud volcanoes
Salinity of water associated with metalliferous deposits
Salinity of waters from sedimentary, metamorphic, and igneous rocks
References

Part 3

Discussion of the Results
General approach
Hydrodynamic zones and geochemistry of water
Correlation
Depth to water
Salinity variation
Regularities
Coefficient of variation
Metamorphism of waters
Chemical relationship of major groups
Coefficient of water exchange
Ionic ratios
Cycle of Metamorphism of Natural Waters
References

"*Tales sunt aquae, qualis terra per quam fluunt*"
Plinius

ABSTRACT*

The problem of the origin, occurrence, and distribution of soluble salts and the formation of chloride brines in the crust of weathering are treated in the present paper as a process caused chiefly by the dynamics of natural waters and the mobility of the chemical constituents dissolved in water.

The hydraulic gradients and velocity of underground flow, the intensity of the water exchange with the earth's surface, the relation of the water-bearing bed to water (e.g., intensive flush, hampered flush, salt accumulation), the subsurface drainage conditions, the duration of time of the contact of water with the geological formations along with the chemical composition of rock material and the water which occurs in them, and the structural features of the area, are considered as the chief factors governing the salinity variation of subterranean waters.

Nearly ten thousand chemical analyses of natural waters, including fresh water and brines, subterranean waters from the numerous artesian basins, oilfield areas, geysers, mud volcanoes, from various sedimentary formations, metamorphic and igneous rocks from the different parts of the globe, have been classified, tabulated, and plotted and considered in this paper.

The relationship between the types of the products of weathering and the major geochemical types of subterranean waters has been found and used for the classification of water.

The variation in salinity of subterranean waters with the change of the hydraulic gradients, with depth of water, with the distance from the outcrops, and with the distance from the sea, have been illustrated by numerous data.

The principles of the distribution of subterranean waters of the different hydrochemical facies (low saline facies, transitional facies, high saline facies) in the crust of weathering in relation to the hydrodynamic zones, salinity concentration, and geological environment (structures, relation to water, depth) are indicated.

The application of the integral frequency curves of the chemical composition of the different types of subterranean waters associated with oil-pools has been demonstrated for practical use in the search for oil.

Ionic ratios $\frac{Cl'}{Mg^{\cdot\cdot}}$; $\frac{SO_4''}{Cl'}$; $\frac{Ca^{\cdot\cdot}}{Mg^{\cdot\cdot}}$; $\frac{Na^{\cdot} + K^{\cdot}}{Na^{\cdot} + K^{\cdot} + Ca^{\cdot\cdot} + Mg^{\cdot\cdot}}$

in subterranean waters and in oceanic water have been treated as the objective criterions showing the origin of highly-concentrated chloride brines.

The metamorphism of natural waters in the crust of weathering is considered as proceeding either in the *normal* course (bicarbonate waters → bicarbonate-chloride waters → chloride-bicarbonate waters → chloride-sulphate or sulphate-chloride waters → sulphate waters →chloride waters), or in the *reverse* course, which is, for the major geochemical groups of water, as follows:

$$\text{bicarbonate waters} \leftarrow \text{sulphate waters} \leftarrow \text{chloride waters}$$

This process is formulated in this paper as the *cycle of metamorphism* of natural waters.

Introduction

Scope of the problem

The origin, accumulation, movement, distribution, and occurrence of subterranean waters in the earth's crust and their salinity variation is undoubtedly one of the

* This paper is being published in three separate parts (i.e., Part 1, Part 2, and Part 3) but this abstract covers all the three parts.

fundamental and important problems of the modern theoretical and applied geology, geochemistry, and geophysics.

The geochemists encountered these phenomena in connection with the solution of the problem of the disturbance of equilibrium and chemical change of rocks and minerals with the ultimate formation of new compounds; the hydraulic geologists and chemists are interested in the estimation of subterranean waters for human consumption; the economic geologists deal with the subterranean waters in the study of genesis and occurrence of the ore deposits; the petroleum geologists and operating engineers, whose interest is concentrated on the behaviour of the fluids in the oil-pools, pay great attention to the role of subterranean water in the driving, accumulation, and distribution of oil in the existing and potential oilfields, as well as to the rate of the encroachment of water when oil is withdrawn.

Furthermore, as the shallow oilfields are depleted the search for deep-seated pools becomes of vital importance, and the problem of subterranean water in the deeper portion of the earth's crust acquires an understandable significance.

While the phenomenon under consideration is of an outstanding scientific and practical interest, the problem of the migration, accumulation, and geochemistry of subterranean waters is still mantled by mystery, contradictions, and confusions.

The complexity of the problem, the insufficiency of information, and the lack of research are in fact the main reasons for the difficulties experienced in the solution of the problem.

The origin of brines associated with many oil-pools has been an especially much discussed subject, and many concepts have been developed to find out the idea about accumulation and distribution of subterranean waters of extremely high salinity.

Although some of the hypotheses provide a reasonable consideration of the process, the problem cannot be considered as yet solved.

The remarkable progress in the study of the structural features of many oil-field areas in the world in last decades, along with the explanation of the process of oil accumulation and distribution, provide in many cases important information related to the occurrence of underground waters in the subsurface reservoirs.

The natural waters in the crust of weathering, similar to all rocks and minerals, are subject to alteration if the physical and chemical environment under which those waters are found changes.

For this reason the main problem in the study of the geochemistry of water is a broad analysis of the dynamic processes in the crust of weathering which govern the variety of the chemical composition of water rather than the quality of water itself as a result of these processes.

From this view point the chemical alteration of waters under natural conditions is treated in the present paper as *metamorphism* of subterranean waters.

Sources of data and principles applied

General notes

This publication is based upon the data collected by the writer's hydrological investigations, as well as from the different published sources, for which the references in each case are given.

The author's investigations related to a number of the artesian basins in Europe

and to the Great Artesian Basin, Pirie-Torrens Basin, and Murray River Basin in Australia.

The information compiled from the published data comprises:

A. The salinity of subterranean waters from:

1. The South Dakota Artesian Basin; 2. Comal County, Texas; 3. The San Diego Area; 4. The Azapa Valley (Chile); 5. The Union of South Africa; 6. The Permian Basin (Ural); 7. New Zealand; 8. Australia (Recent-Pleistocene and Tertiary formations); 9. Crystalline and metamorphic rocks of Central Asia; 10. Eastern Kentucky natural brines; 11. Joplin zinc and lead deposits (U.S.A.).

B. The following oilfield areas:

1. U.S.A.—Rocky Mountain, Appalachian, Oklahoma-Kansas, California, Texas, Louisiana; 2. Canada—Alberta Province; 3. Other countries—Germany, Rumania, Russia, Burma, Venezuela.

C. Subterranean waters of volcanic association:

1. Geysers, Nevada; 2. The Turkmenian mud volcanoes.

The main purpose of this paper is to treat the problem of the occurrence and metamorphism of salinity of natural waters in the crust of weathering from the viewpoint of the modern hydraulics of subterranean waters, and the relative mobility of the chemical elements.

9,719 chemical analyses of subterranean waters and 3,364 bores showing the depth of water collected practically from all the continents have been classified, collated, and considered in this paper.

The geochemical types of subterranean waters along with the hydrodynamic classification of the subsurface reservoirs have been developed and applied for the treatment of the problem.

The application of the methods of the mathematical analysis and the integral frequency curves enable the writer to cope with the numerical factual data related to the depth of occurrence and salinity distribution of water, chiefly those associated with oil-pools.

This has greatly simplified the problems of the correlation of water of different regions or from various depths in the same area and more effective utilization of the data for practical use.

Most of the evidence upon which the ideas were derived are based on the study of the mass-assorted data related to the wide variety of subterranean waters along with the geological and geochemical conditions.

This paper is actually a scientific result of work of many years in the field of hydrology of subterranean waters and geochemistry of soluble salts.

The author, however, does not assume that this contribution either covers all the subject or treats all the aspects of the problem with equal detail, but it is believed that the present study brings to light the basic processes involved in the mechanism governing the chemical change of water in the subsurface reservoirs and frames new ideas related to this phenomenon.

Frequency curves

The principles of the theory of frequency and mathematical statistics as they were described elsewhere (Chebotarev, 1951) have been used in this paper for the computation of the assorted data.

Arranging the data available in either increasing or decreasing order, we can compile a "table of distribution" of the statistical aggregates.

For example, the total number of items is 920 (Table 1).

Table 1. *Computation of the data required for the plotting of frequency curve for depth to water (South Australian portion of the Great Artesian Basin)*

Rating of depth (feet)	x_z	y		z	z^2	zy	z^2y
		n	%				
0–1,000	500	818	89·0	0	0	0	0
1,000–2,000	1,500	83	9·1	1	1	83	83
2,000–3,000	2,500	6	0·6	2	4	12	24
3,000–4,000	3,500	10	1·0	3	9	30	90
4,000–5,000	4,500	2	0·2	4	16	8	32
5,000–6,000	5,500	1	0·1	5	25	5	25
d = 1,000	—	920	100·0	—	—	138	254

Grouping them at certain intervals and computing the required data, we will have all the necessary information for the plotting of the empirical (distribution) and integral frequency curves. For the computation, the following denotations have been accepted:—

d is the length of interval;

x is a variant of the statistical distribution;

x_0 is a variant corresponding to the zero interval;

z is numbers of the intervals counting from the zero interval;

x_z is a value of x corresponding to the middle of zth interval;

$$x_z = x_0 + z \,.\, d;$$

y is frequency of the x_z interval ($\Sigma y = n$);

$$v_1 = \frac{\Sigma zy}{n} = \frac{138}{920} = 0{\cdot}15; \quad v_2 = \frac{\Sigma z^2 y}{n} = \frac{254}{920} = 0{\cdot}27;$$

$$\mu_1 = x_0 + v_1 \,.\, d = 500 + 0{\cdot}15 \,.\, 1{,}000 = 650 = \bar{x};$$

$$\mu_2 = d^2(v_2 - v_1{}^2) = 1{,}000{,}000(0{\cdot}27 - 0{\cdot}15^2) = 247{,}500; \quad \sqrt{\mu_2} = 497 = \sigma.$$

μ_1 is the first statistical moment which presents an average ($\bar{x}$) of distribution;

μ_2 is the second statistical moment which equals σ^2 or

$\sqrt{\mu_2} = \sigma$, where σ is the standard deviation.

Arranging on the axis of ordinate the value of frequency (y) and on the axis of

abscissa the interval of the depth, we will have an empirical frequency (distribution) curve for a given statistical distribution.

For the plotting of the integral frequency curves, coefficient of variation $\left(C_v = \frac{\mu_2}{\mu_1}\right)$ and coefficient of skew (C_s) must be computed and then the ordinates of the integral curve can be found (Foster's method) (Chebotarev, 1951).

The C_v value has the following significance: that C_v is greater, the more the variety of the variants of the distribution, and vice versa. When the magnitude of C_v is greater, the end parts of the integral curve will deviate more from the centre of distribution $\left(\frac{x}{\bar{x}} = 1\right)$.

For the purpose of this paper it is possible to take into account only the most characteristic frequency (percentage) namely: 1 per cent, 10 per cent, 25 per cent, 50 per cent, 75 per cent, 90 per cent, and 99 per cent.

Ionic ratios

On the basis of the data related to the chemical composition of the various groups of subterranean waters which are considered in this paper, the following

Table 2. Ionic ratios (reacting values in percent) of certain anions and cations which occur in subterranean waters

Ionic ratios	*Oceanic water*	*Relative mobility*
$\frac{Cl'}{Mg^{\cdot\cdot}}$	5·08	77·0
$\frac{SO_4''}{Cl'}$	0·10	0·57
$\frac{Ca^{\cdot\cdot}}{Mg^{\cdot\cdot}}$	0·20	2·30
$\frac{Na^{\cdot} + K^{\cdot}}{Na^{\cdot} + K^{\cdot} + Ca^{\cdot\cdot} + Mg^{\cdot\cdot}}$	0·79	—

ionic ratios of the anions and cations (in reacting values per cent) have been computed and used as a criterion for the correlation of waters.

$$\frac{Cl'}{Mg^{\cdot\cdot}}; \quad \frac{SO_4''}{Cl'}; \quad \frac{Ca^{\cdot\cdot}}{Mg^{\cdot\cdot}}; \quad \frac{Na^{\cdot} + K^{\cdot}}{Na^{\cdot} + K^{\cdot} + Ca^{\cdot\cdot} + Mg^{\cdot\cdot}}$$

The relative mobility of these ingredients in the earth's crust (Table 4) and their abundance in the oceanic water (Table 10) are assumed to be the most indicative (Table 2).

Acknowledgements

The consideration of the problem in question in its present aspect has been possible owing to the valuable contributions by numerous scientists throughout the world,

and particularly to the American and Russian geologists, hydrologists, and petroleum chemists.

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In carrying out the present study, the author had the valuable advice of the late Professor B. B. Polynov, whose brilliant ideas, erudition, and amicable attitude have encouraged the author's investigation for a number of years.

It is, therefore, my honourable duty to dedicate this contribution to his memory.

Theoretical Aspect

Previous concepts

The problem of the occurrence, chemical change, and salinity concentration in subterranean waters in the crust of weathering generally, and the association of chloride brines with petroleum and natural gas in particular, has puzzled geologists for a long time.

Because this phenomenon is of general interest and of the utmost practical importance, a number of hypotheses have been proposed to solve the problem.

Some of these hypotheses seem to be fairly well grounded, while other ones are entirely deductive, being postulated merely to explain certain observed features.

"Connate" waters

The term "connate" waters is applied to "waters laid down with the strata when they were laid down" or "buried with the beds in the first place" (Lane, 1908; Washburne, 1914).

These waters are also termed "fossilized brines" (Washburne, 1915). It is assumed that "connate" waters may be marine or fresh, but typically they are stagnant waters.

It was suggested that "connate" waters occur in free or occluded state, in solid solution, or in chemical combination (Daly, 1917).

Theoretically speaking, it is unlikely that anyone will deny the occurrence of the buried waters in some sedimentary formations in the earth's crust, but as the information about this water has accumulated it has become evident that most "connate" waters have been so altered in composition by many chemical and physical processes such as absorption, evaporation, dilution, base exchange,

hydration, sulphate reduction, and other processes, that "they do not represent at all accurately the original water of deposition" (Rubey, 1951).

Hypothesis that brines are concentrated by evaporation in gas

This concept is based on the assumption that subterranean waters undergo deep-seated concentration, brought about by their evaporation into moving and expanding gas (Mills and Wells, 1919).

Undoubtedly it is theoretically possible that some of the brines found in sedimentary rocks have been concentrated under certain conditions to some degree by evaporation into gases generated in bituminous shales, but the extensive occurrences of the brines in the earth's crust could not be formed by this process.

Condensation of capillary water

It is supposed (Buneev, 1944; Russell, 1933; Washburne, 1915) that gas saturated with water, being in contact with capillary pores in certain sedimentary beds, will cause the formation of condensation water. This water migrates after that under capillary movement.

The error of this concept is evident from the point of view of the theories of capillarity.

Indeed, one knows that capillary movement of water is almost exclusively limited by the sediments which lie above the surface of saturation, and it is improbable that this process may play any significant role in the origin of brines.

Other hypotheses

The formation of brines either due to gravitational molecular settling under the action of osmosis and diffusion phenomenon, or by hydration of minerals or absorption of salts from solution by very fine sediments during deposition, can hardly explain the magnitude and universal occurrence of brines.

Although these hypotheses are grounded upon the well-known principles of physics and chemistry, the role and the scale of the processes even in the course of geological time would be inadequate to explain their importance as a decisive agency in the concentration and amount of chloride brines occurring in the earth's crust.

Migration of soluble salts

Cycle of weathering

When attempting to discover the chief principles governing the change in salinity of natural waters in the earth's crust we must take into account the cycloidal migration of the chemical elements in the crust of weathering, that is, the lithosphere, the hydrosphere, and the atmosphere.

The crust of weathering is treated as the "upper part of the lithosphere, which consists of the loose products of the disintegration of igneous and metamorphic rocks" (Polynov, 1937). It is believed that the uppermost thin earth's crust is as great as ten miles (Fig. 1).

The transference and transformation of the solid substance to the state of dispersion which may take place in a gaseous as well as in a liquid medium, leads

gradually to the breaking-up of the molecules into chemical ions. Further changes in structure and texture of the substance are treated as being essentially a base-exchange process (Frederickson, 1951).

Indeed, the alteration of material in the crust of weathering is a complicated series of unceasing physical-chemical reactions which are primarily determined by the varying mobility of the chemical elements and compounds and their ability to react with each other.

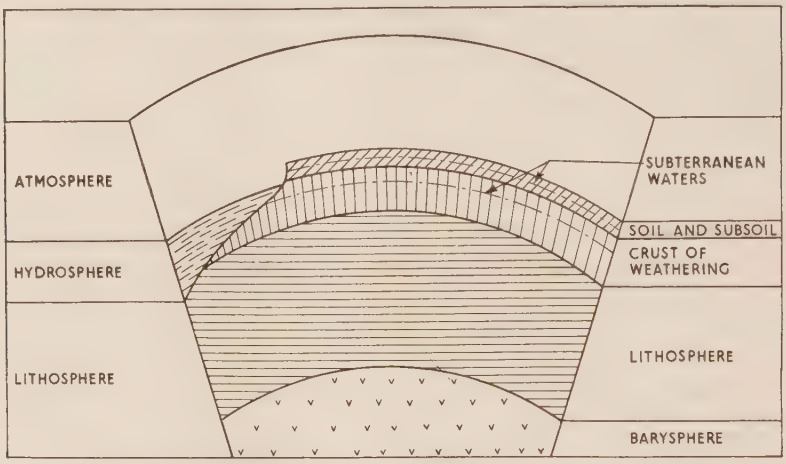

Fig. 1. Diagram showing position of subterranean water in rélation to the elements of the earth's sheath.

It has been stated that for each kg of sea-water, about 600 g of primary rocks have passed through the cycle of weathering, disintegration, and sedimentation (Goldschmidt, 1937).

There are a series of the transitional types of the products of weathering between solid rock and the state of its dispersion.

Nevertheless, two major groups of the products of weathering in the earth's crust can be determined, namely the *residual* products and the *accumulative* products.

In turn, each of these groups comprises a number of the various formations whose genetic type and geochemical character are determined by the correspondent *cycle* of weathering. (Polynov, 1937.)

The transformation of material is, of course, a dynamic process, and it can hardly be expected that an equilibrium between the residual and accumulative products may be observed in nature.

By contrast, the well-known geological factors such as the tectonic movements and the epeirogenetic fluctuations involving vast areas of the earth's crust, volcanic activity, disintegrating and decomposing action of surface and underground water and atmospheric agents on the rocks and minerals (oxidation, carbonation, and hydration processes), the activity of organisms, and the formation of organic compounds create an interrupted chain of geochemical alteration in the earth's crust. This is actually a series of the successive evolutionary cycles. For this reason the relationship of the cycles of weathering to the types of the products

of weathering can be fixed only according to the predominance of certain types of the products of weathering occurring in the earth's crust.

As a matter of fact, the first cycle of weathering (orthoeluvium) can be considered as an "entire" one, since igneous and highly metamorphosed rocks, being a subject of change in structure and texture produce, after all, the main types of residual (detrital, siallitic, and allitic) products as well as accumulative (chloride, sulphate, calcareous, and siallitic) products. (Table 3 and Fig. 2.)

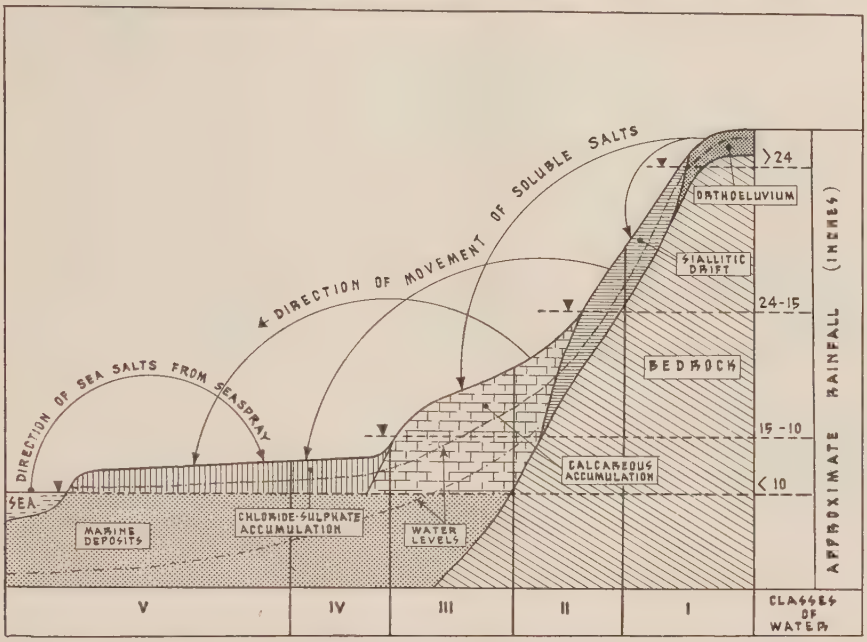

Fig. 2. Diagram showing relationship of subterranean waters to products of weathering, rainfall, and drainage conditions.

In other words, very complex physical and chemical processes govern the change and the redistribution of the substance in the earth's crust: the dispersion, disintegration, differentiation with the simultaneous separation, concentration, integration, and the formation of new compounds take place.

*Mobility of soluble salts**

Chief ingredients—According to the electrolytic dissociation theory, the soluble salts which occur in solution (water) are in the state of ions, and the number of positive ions expressed in the reacting values must be equal to the number of negative ions of the same value.

The weaker the concentration of the solution the stronger is the degree of the dissociation, particularly when strong acids and bases occur.

The amount of positive ions (cations) and negative ions (anions) can be used as a measure for the total salinity of water (solution).

* The term "mobility of soluble salts" is applied here as a synonym of the ions' migration ability in the great hypergenetic cycle but not as a criterion of their chemical mobility.

Table 3. Cycles and types of products of weathering (modified from Polynov, 1937)

Cycles of weathering	*First cycle (Orthoeluvium)*		*Second cycle (Paraeluvium)*		*Third cycle (Neoluvium)*	
	Residual products	*Accumulative products*	*Residual products*	*Accumulative products*	*Residual products*	*Accumulative products*
Types of products of weathering	1. Coarse Detrital	1. Chloride-sulphate (chiefly alluvial)	1. Detrital	1. Chloride-sulphate	1. Solonez and Gypsum bearing	1. Chloride-sulphate
	2. Calcareous (under vegetation cover)	2. Calcareous (chiefly colluvial and proluvial)	2. Siallitic (supracalcareous)	2. (a) Calcareous (b) Chloride-sulphate	2. Leached supracalcareous (siallitic)	2. $CaCO_3$
	3. Siallitic*	3. Siallitic	3. Allitic (?)	3. (a) Siallitic (b) Calcareous (c) Chloride-sulphate	3. Unsaturated siallitic‡	3. Alumino- and ferri-siliceous system
	4. Allitic† (lateritic crust of weathering)					
Types of rocks	Igneous (and highly metamorphosed)		Sedimentary		Recent Drift	

Remarks: * A large quantity of silica and much of its calcium and sodium compounds are removed; the aluminosilicates pass gradually into residual aluminosilicic acids, i.e., acids of the kaolin type.
† The accumulation of sesquioxides at the expense of the leaching out of the alkalis, alkaline earth, and silica.
‡ The action of carbonated atmospheric water is insufficient to replace the absorbed ions by hydrogen.

Fig. 3. Orthoeluvium upon metamorphic rocks (Australia). (Author's photo.)

Fig. 4. Calcareous drift (loess, East Europe). (Author's photo.)

Fig. 5. Nodular travertine (a geochemical variety of calcareous drift) (Australia). (Author's photo.)

Fig. 6. Zone of chloride-sulphate accumulation (Australia). (Author's photo.)

From about eighty chemical elements recognised in the earth's crust, the following chief constituents are considered as forming the water-soluble salts:—

Cations

Group A: $Na^{\cdot}$, $K^{\cdot}$, $Ca^{\cdot\cdot}$, $Mg^{\cdot\cdot}$, $H^{\cdot}$

Group B: $NH_4^{\cdot}$, $Al^{\cdot\cdot\cdot}$, $Fe^{\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, etc.

Anions

Group A: HCO_3', CO_3'', Cl', SO_4''

Group B: NO_2', NO_3', SO_3'', OH', F', SiO_3'', etc.

Group A comprises those ions which are constantly present in water, often in considerable quantity, and the occurrence of which determines the physical properties and the geochemical type of water.

Group B consists of ions of the subordinate importance, because they either are found in very small quantities or their occurrence in water is not constant.

Goldschmidt (1937) suggested that the chemical behaviour of many elements, especially those connected with aqueous solutions in the earth's crust, might be predicted when they are grouped according to their, so-called, *ionic potential*, that is, the ratio of the ionic radius of the elements and the ionic charge (valency) are known.

He states that "substances with low ionic potential, such as sodium, calcium, and magnesium, remain in true ionic solution in the process of weathering and transportation; those with intermediate ionic potential are precipitated by hydrolysis, their ions being associated with hydroxyl radicals from equeous solutions; and substance with still higher ionic potential form anions containing oxygen and usually again soluble to give true ionic solution."

Mobility of ions

The action of water as a dissolvent of rock and minerals is accompanied by chemical reactions, and although these reactions are sometimes slow, they impel the breaking of the equilibrium of the inert mass of rocks and minerals.

The occurrence, differentiation, and regrouping of the chemical elements in the earth's crust are determined primarily by their mobility, that is, the ability to pass into ionic solution in water.

The laws of the cycloidal migration of the chemical elements in the earth's crust show that definite and uninterrupted processes differentiating and redistributing the chemical compounds take place in the products of weathering.

The degree of dispersion of material and the magnitude of the transporting forces are the factors of great significance. The base-exchange property of clay minerals, i.e., their ability to exchange certain cations for other cations in solution, is a very important phenomenon determining the mobility of the chemical elements.

The following relative exchange property of the cations in the clay mineral (montmorillonites) has been stated (Ronov, 1945):

$$Na < H < K < Mg < Ca.$$

In the Atlantic and Gold Coasts, for instance, base-exchange in natural waters is considered as a factor governing their salinity concentration (Foster, 1942).

The interaction of the soluble components occurring in the products of weathering with moving surface and underground water facilitates transportation of them to the sea and other natural depressions.

The data in Table 4 show the average chemical composition of igneous rock and mineral residual of river and oceanic waters.

Table 4. Average composition of igneous rocks and mineral residual of river and oceanic waters (Polynov, 1937) (*per cent*)

Elements and compounds	*Average composition*			*Relative mobility of elements (columns 2 and 3)**
	Igneous rocks	*Mineral residue of*		
		river waters	*oceanic waters*	
1	2	3	4	5
SiO_2	59·09	12·80	—	0·20
Al_2O_3	15·35	0·90	—	0·02
Fe_2O_3	7·29	0·40	—	0·04
Ca	3·60	14·70	1·19	3·00
Mg	2·11	4·90	3·72	1·30
Na	2·97	9·50	30·59	2·40
K	2·57	4·40	1·10	1·25
Cl	0·05	6·75	55·29	100·00
SO_4	0·15	11·60	7·69	57·00
CO_3	—	36·50	0·20	—

* *Remarks:* These are the ratios of percentage of Cl content to any other ions and compounds (I. Ch.).

It is easy to see that while the quantity of chloride in fresh primary rocks hardly rises to 0·05 per cent, in river waters it can be as large as 6·75 per cent and in oceanic water its content is as great as 55·29 per cent.

This fact is clear evidence that the considerable increase of Cl-ion in the river and oceanic waters is due to the relative ease with which this element goes into solution.

Regrouping the data shown in Table 4 (fifth column), the following four phases of the solution and redistribution of the chemical elements in the earth's crust can be found (Fig. 7).

This sequence of the phases is in full conformity with the properties of the chief compounds, which dispose themselves as follows: chlorides and sulphates in nature are ten times that of calcium, sodium, magnesium, and potassium, whose mobility is, in turn, one hundred times that of iron and aluminium. On the other hand, calcium precipitates nearly five times more rapidly from water than magnesium, whereas the content of sodium, which is most soluble, is usually higher than that of the potassium ion. The Ca, Mg, Na, and K content in the solutions circulating in the crust of weathering may be substantially changed under the

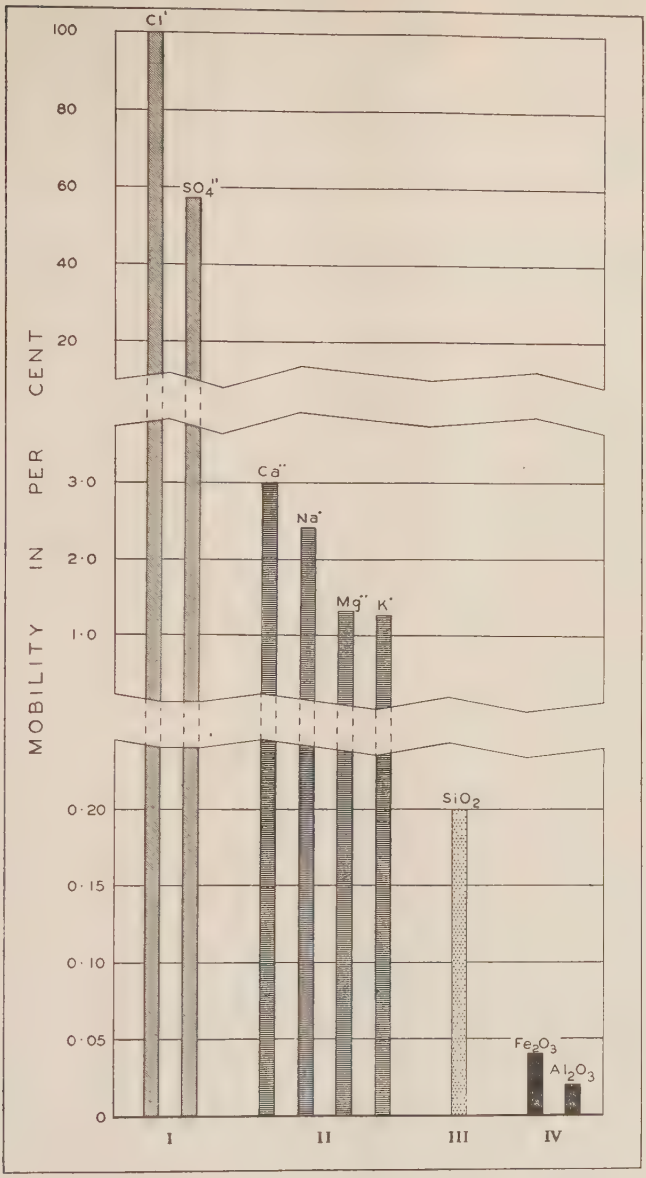

Fig. 7. Diagram showing phases of weathering (I, II, III, IV) and relative mobility of chemical elements and compounds.

action of organisms, base-exchange process, and precipitation as salts from the saturated solutions. The reaction of natural waters with carbon dioxide causes the formation of carbonic acid, which originates ion of hydrogen ($H^{\cdot}$) and bicarbonate (HCO_3) as follows:

$$H_2O + CO_2 \rightleftarrows H_2CO_3 \rightleftarrows H^{\cdot} + HCO'_3$$

This process plays a very important role in the metamorphism of subterranean waters.

It is realized that the area where the process of migration of the soluble salts starts under the subaerial weathering is the zone of the residual products, although a further stage in this process involves the next low-lying zones of siallitic drift and calcareous accumulation (Fig. 2).

It should be also noted that early in the process of weathering, underground water is charged by the more soluble salts. Later the less mobile chemical elements increase.

All chlorides which pass into solution from any source remain in solution, whereas sulphates and particularly carbonates easily precipitate from the solutions.

Chemical relationship of rock to water

Plinius' philosophical concept that "*Tales sunt aquae, qualis terra per quam fluunt*" (waters take their nature from the strata through which they flow) retains nowadays its profound sense, and it is found to be in full conformity with the modern interpretation of the chemical relationships of rock to water.

Although practically all the minerals which are found in the earth's crust, namely, stable primary minerals of parent rock, stable secondary minerals (kaoline type) formed by chemical decay of the unstable primary minerals, and the precipitated chemical compounds, are soluble to some degree in natural water, the secondary products and precipitates are of a great importance to the geochemistry of subterranean waters.

The mineral composition of the average igneous rock and the average sediment reveal that whole quartz, carbonates, kaolin, limonite, chlorine, etc., substantially increase under the weathering process, the ferromagnesian constituents of the igneous rocks either are destroyed or appear as new minerals and compounds in the sediments.

Natural waters in the presence of carbonic acid and oxygen act as decomposing and solvent agents in the earth's crust, and this action is due either to the water itself or to the dissolved substances.

In the first stage of decomposition of the silicates, for instance, a large amount of chlorides, sulphates, alkalies, alkaline earths are lost. The water, being saturated by CO_2, affects the disintegrated rocks actively (Table 5).

In turn the waters cannot remain unchanged in their chemical composition, as they are in contact with soluble material, but the proportion and the type of soluble matter taken up from the rock material depends on a number of factors.

Generally the chemical relationship of rock to water is determined by:—

1. The kind of the geological formations;
2. The structural feature of the area;
3. The temperature of water;
4. The salinity concentration and the abundance of particular ions and compounds in water;
5. The amount of water moving through;
6. The velocity of flow.

Table 5. Solubility of the different compounds of the rocks and minerals under the action of water saturated by CO_2 (Daikuhara)

Compounds	Granite		Gneiss		Basalt		Hornblende		Mica	
	a	*c*	*a*	*c*	*a*	*c*	*a*	*c*	*a*	*c*
CaO	0·417	21·147	0·418	16·076	0·350	9·090	0·679	7·316	0·461	30·733
MgO	0·409	65·967	0·389	19·846	0·373	44·939	0·498	18·601	0·337	42·125
K_2O	0·070	0·892	0·084	1·476	0·070	2·052	0·071	2·040	0·082	0·784
Na_2O	0·782	16·963	0·792	18·290	0·709	13·847	1·134	15·793	0·816	13·035

Note: The experiment lasted one hundred days. The rocks have been broken into pieces and the solution above the sediment has been poured off fifteen times (i.e., every seven days) and was kept for the analysis; in its place the equal quantity of water saturated by CO_2 has been poured in.

a—the content of the oxides in the solution;

c—the soluble part in percent in relation to gross weight of the oxides in the primary rocks and minerals.

Thus, the dissolved constituents in natural waters originate chiefly from rock-weathering, but cementation and diagenetic changes in sediments, particularly those of an earlier stage, may add to or reduce the elements and compounds from the circulating underground water.

The abstraction of silica, lime, iron salts, etc., from the underground waters is one of the processes which play an important role in cementation of rocks.

The solvent action of the rapidly moving water of low salinity is usually much greater than that of slowly moving water of higher salinity concentration.

By contrast, when the underground waters are in the active exchange with the earth's surface (see further), that is, when the abundant water circulates rapidly, its salinity concentration is less than in water which moves slowly (delayed water exchange).

In deeper portions of the geological structures where the stagnant conditions prevail the water of high concentration is usually found regardless of the nature of the formation in which this water occurs.

All the chlorine and most of sodium which pass into solution tend to stay there, augmenting the salt-content in water, while most of carbonates precipitate from the solution and are replaced by chlorine or sulphate ions.

It is assumed that chlorine in sedimentary rocks, where it may be found in the state of dispersion, in solution, and in salt beds, to be small compared to oceanic chlorine (Kuroda and Sandell, 1953). The dilution, blend, and chemical contamination of waters from other sources in the subsurface reservoir are an integral part of the dynamic relation of rocks and natural waters.

The principal reason in salinity variation in subterranean waters from this viewpoint is to be found in the different properties and ability of the rocks to contribute to the dissolved mineral content of the circulating water.

While certain substances are vigorously affected by water and pass rapidly into solution, other chemical compounds are more resistive against the weathering process, and for this reason the chemical composition of natural water may differ widely from place to place.

Table 6. Loss and gain of ions and chemical compounds (per cent) under the weathering process (O'Shannassy Catchment, Victoria, Australia) (Anderson, 1940)

Ions and compounds	*Unaltered dacite*	*Weathered (friable) dacite*	*Red soil derived from dacite*	*Difference (per cent)*		*Type of products of weathering*
				Loss	*Gain*	
1	2	3	4	5	6	7
SiO_2	63·32	56·87	50·49	20·3	—	
Al_2O_3	16·30	25·23	22·73	—	39·0	Allitic
Fe_2O_3	0·13	5·91	7·30	—	5·5	
FeO	6·29	0·97	2·60	59·0	—	
MgO	2·89	1·45	0·77	73·1	—	
CaO	4·23	0·28	0·38	91·0	—	
Na_2O	2·22	0·27	Trace	88·0	—	
K_2O	3·28	0·67	0·67	80·0	—	
Cl	0·025	0·08	0·052	—	108·0	

Remarks: Figures in graphs 5, 6, and 7 have been computed by the present author.

Table 7. Losses by weathering of average igneous rock compared with dissolved mineral content of Ottawa River (Leith *and* Mead, 1915)

Compounds	*Losses by weathering of average igneous rock*	*Ottawa River at Ottawa*
SiO_2	63·28	30·20
Al_2O_3, Fe_2O_3	2·71	10·75
MgO	6·53	11·90
CaO	13·36	35·00
Na_2O	8·85	9·18
K_2O	6·27	2·88
Total	100·00	—

The occurrence of the saline formations in the rocks of different ages which are found in many areas of the world (in Ohio, for instance) (Bownocker, 1906), is a factor of great importance in the formation of highly concentrated subterranean waters.

In the Upper Permian sediments in the Northern Volga Basin, gypsum and rock-salt horizons bring about a high concentration of soluble material in waters, while in limestone, dolomites, marls, the red sandstone, and clay, etc., the salt concentration in the water is low (Afanas'ev, 1949).

Although the loss of the soluble constituents by the rocks corresponds in many instances with the gain of dissolved matter in water, it can hardly be expected that

Table 8. Chemical composition of surface waters associated with different rocks at various levels, Victoria, Australia (Anderson, 1945)

Type of stream	*Altitude above S.L. (feet)*	*Type of rock*	*Locality*	*p.p.m.*							
				Na	K	Ca	Mg	Cl	SO_4	HCO_3	NO_3
High level streams	6,000	Ordovician	Mt. Hotham	1·5	0·6	1·4	0·6	0·9	0·2	7·8	2·2
	4,000	Granite	Buffalo Plateau	0·9	1·1	0·7	0·2	1·2	0·4	3·6	0·8
	—	Schists	Bogong High Plains	1·05	0·77	0·95	0·42	0·93	0·29	4·90	0·44
Comparatively low level streams ("valley tracts" and "plain tracts")	—	—	Near Bright Rose River	5·2		4·3	4·9	2·8	2·5	43·6	Nil
	—		Near Dondangadale	3·2		2·2	1·5	2·9	1·7	21·2	Nil
	—		Murray River at Tocumwal	2·4	1·0	3·9	2·1	3·4	1·3	23·0	Trace
Saline streams in W. Victoria	—	—	—	726		180	116	1,390	134	490	Nil

amount of soluble salts and the ionic content in water may correspond exactly with the total losses from the weathered rocks. The analyses of unaltered and weathered rocks (Tables 6, 7, 8), along with the data showing the salinity concentration of water associated with different rocks (Tables 17, 18, 19), illustrate the chemical relationship of rock to water.

Geochemistry of subterranean waters

Motion of water

Natural waters in the subsurface reservoirs, similar to those of the ocean and of the atmosphere, are never at rest.

As it was pointed out elsewhere (Chebotarev, 1953), subterranean waters, obeying the law of fluids, always move from a point of high head towards one of

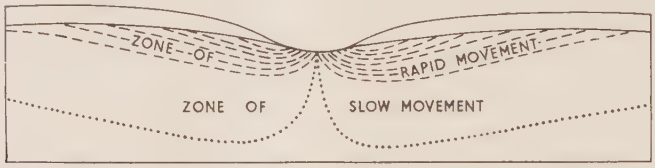

Fig. 8. Diagram showing concentration of motion in underground water (Fuller, 1911).

low head. The behaviour of these waters at rest and in motion is largely dependent on gravitational and the mechanical forces applied to water.

The type of water-bearing formation, the shape and size of grains, the occurrence of structural and solution openings (Table 9), the relationship between moving water and the material, the difference in elevations between water in the intake and outlet zones, and the physical and chemical properties of water itself,

Table 9. Relationship of various types of rocks in which water occurs in structural and solution openings to topographic locations of wells and to their average yield (Ellis, 1909)

Type of rocks	*Topographic location*	*Average yield of well for location*
Granite	hills	9·3
	slopes	10·3
	valleys	21·7
Schist	hills	20·0
	slopes	8·7
	valleys	24·4
Gneiss	hills	21·8
	slopes	10·1
	valleys	24·3
Other crystalline rocks	hills	21·7
	slopes	2·2
	valleys	42·5

are among the factors which determine the hydraulic properties of the aquifer and salinity of subterranean waters.

In other words, the hydraulic gradient and the permeability of the water-bearing formation are chief agents influencing the motion of natural waters in the earth's crust.

The movement of water in the subsurface reservoir must always have been associated with the crust deformation and rock consolidation, particularly in the highly compact rocks.

It has been suggested that "if hot springs are delivering to the surface an average of only 0·8 per cent of juvenile water, they could in the course of geologic time, account for the entire volume of the ocean" (RUBEY, 1951), and that "the hydrosphere was obtained from the interior of the earth through geological time" (KULP, 1951).

Geochemical classification of waters

From the geochemical viewpoint, all natural waters are the dynamic aqueous solutions of soluble salts, the amount of which depends on the origin of water, its movement, the presence of soluble salts in the sediments through which it passes, the drainage conditions, and the position of a given place in relation to the geochemical zones, etc.

Changes in these conditions disturb the equilibrium of the solution, and a new form of equilibrium which would be stable in a given surrounding arises.

The chemical characteristics of subterranean waters suggesting their origin and the natural environment of their occurrence may be termed as the *genetic characteristics* of waters, whereas the types of water that can be identified on the basis of such characteristics may be treated as the *genetic types* of subterranean waters (CHEBOTAREV, 1950).

Although the general mineralization (total salinity) of subterranean waters varies considerably, the types of the soluble salts remain largely unchangeable. On the other hand, the similarity in chemical composition of subterranean waters can be revealed under widely different natural conditions, but in most cases the analogous hydrodynamic environment for the waters of the similar chemical properties can be recognized.

The ions which occur in natural waters are rather numerous, but only a few of them (HCO_3', CO_3'', Cl', SO_4'', $Na^{\cdot} + K^{\cdot}$, $Ca^{\cdot\cdot}$, $Mg^{\cdot\cdot}$) have been taken into consideration with a view to determining and expressing the possible chemical reactions and properties of water.

The fundamental assumption is that anions are independent ingredients, while cations are dependent variables, and the major geochemical groups of waters are therefore those determined by the occurrence and prevalence of the former ones.

The following three major categories of natural waters which practically cover all the variety of the chemical composition of subterranean waters have been subdivided: (1) the *bicarbonate* waters, (2) *sulphate* waters, and (3) *chloride* waters.

The waters containing free sulphuric and hydrochloric acids in solution, that is, the "acid" waters, have been left out from the consideration.

In general, in the area located between a water-divide and the basis of the

Table 10. *Geochemical classification of subterranean waters*

A. *Relationship of the products of weathering to the genetic types of water*

Presumable phase of weathering	*Products of weathering*	*Genetic types of water*
Fourth phase	Residual (orthoeluvium and detrital paraeluvium)	Bicarbonate (alkaline)
Third and partly Second phases	Siallitic drift	Bicarbonate-chloride (alkaline-saline)
Second and partly First phases	Calcareous accumulation	Chloride-bicarbonate (saline-alkaline)
First phase	Chloride-sulphate accumulation	Chlorine-sulphate (saline)
		Chloride (saline)

B. *Geochemical groups of waters*

Major group of water	*Diagram symbol (Fig. 2)*	*Genetic types of water*	*Reacting value in per cent*						
			$HCO_3' + CO_3''$	Cl'	SO_4''	$Cl' + SO_4''$	$HCO_3' + Cl'$	$HCO_3' + SO_4''$	*Cations (in oilfield waters)*
Bicarbonate	I	Bicarbonate	Greater than 40	—	—	Less than 10		—	$Na^{\cdot} + K^{\cdot}$ prevail in all types of waters.
	II	Bicarbonate-chloride	40–30	—	—	10–20		—	$Ca^{\cdot\cdot}$ and $Mg^{\cdot\cdot}$ less than 2·5 in the water of high saline facies and less than 19·0 in low saline facies (Table 33)
	III	Chloride-bicarbonate	30–15	—	—	20–35		—	
Sulphate	IV	Sulphate-chloride	15–5	Less than 25	Greater than 25	—	—		$Na^{\cdot} + K^{\cdot}$ prevail in all types of waters.
		Sulphate	—	—	Greater than 40	—	Less than 10	—	$Ca^{\cdot\cdot}$ less than 4·5 in all waters. $Mg^{\cdot\cdot}$ less than 4·0 in all waters (Table 36)
Chloride	III	Chloride-bicarbonate	30–15	Greater than 20	—	—	—	—	$Na^{\cdot} + K^{\cdot}$ prevail in all types of waters.
	IV	Chloride-sulphate	15–5	Greater than 20	—	—	—	Less than 25	$Ca^{\cdot\cdot}$ less than 12·5 in the water of high saline facies.
	V	Chloride	Less than 5	Greater than 40	—	—	—	Less than 10	$Mg^{\cdot\cdot}$ less than 6·0 in all types of waters (Table 37).

erosion the following relationship between the types of the products of weathering and genetic types of subterranean waters can be drawn (Table 10 and Fig. 2).

The representative characteristics of each type of subterranean water in comparison with fresh-lake and oceanic water are given in Table 11.

Table 11. *Representative waters of different genetic types in comparison with fresh-lake and oceanic waters*

Type of water	*Class of water*	*Total salinity (p.p.m.)*	*Reacting value in per cent*						*References*
			Na + K	Ca	Mg	Cl	SO_4	$HCO_3 + CO_3$	
Alpine lake water	—	22·9	15·1	31·2	3·7	9·2	8·1	32·7	12
Bicarbonate water	I	387·4	5·3	28·7	16·0	5·4	2·8	41·8	34
Bicarbonate-chloride water	II	4,842	47·0	1·1	1·9	13·6	0·4	36·0	13
Chloride-bicarbonate water	III	4,710	41·2	5·0	3·8	23·7	9·8	16·5	13
Chloride-sulphate water	IV	8,953	25·5	13·8	10·7	5·4	37·1	7·5	13
Chloride water	V	162,890	32·7	12·9	4·4	50·0	0	0	35
Oceanic water	—	35,000	39·3	1·8	8·9	45·2	4·6	0·2	11

Relationship of salt to fresh water

Classification of waters—The terms "fresh water" and "salt water" are rather of conventional nature, but generally it is assumed the salt water has a brackish taste.

From the geochemical viewpoint a variety of natural waters falls into three main classes (Valiashko, 1939; Vernadsky, 1933).

Fresh water with a concentration of the solution up to 10,000 p.p.m.

Salinized water with a concentration of the solution from 10,000 to 35,000 p.p.m.

Saline water (brine) with a concentration of the solution from 35,000 p.p.m. and up.

The upper boundary for "fresh water" (i.e., 10,000 p.p.m.) has been determined mainly on the biological-geochemical basis: this boundary is considered as corresponding to the limit below which the natural fresh-water fauna and flora are known to be completely different from natural life in salt-water bodies.

It is also believed that above this concentration hydrated complexes prevail in the aqueous solution.

The upper limit for "salinized water" is that corresponding to the salinity concentration of oceanic water, which is considered as the criterion for the distinguishing of these waters from "saline waters" (brines).

From the practical viewpoint, that is, for the evaluation of water for human consumption, the following groups of water can be allotted: fresh water, brackish water, salt water, and extremely salt water (Table 12).

Equilibrium of waters—Natural waters of higher salinity concentration have normally a higher specific gravity than that of fresh water, and they always tend to occupy either the lower portion of the aquifer or the deepest section of the structural unit.

Table 12. *Qualitative groups of natural waters* (*Author's data*)

Qualitative groups		*Approximate salinity p.p.m.*
Major groups	*Subdivisions*	
Fresh water	Good potable	Less than 500
	Fresh	Less than 700
	Fairly fresh	700–1,500
	Passably fresh	1,500–2,500
Brackish water	Slightly brackish	2,500–3,200
	Brackish	3,200–4,000
	Definitely brackish (limit for human consumption)	4,000–5,000*
Salt water	Slightly salt	5,000–6,500
	Salt	6,500–7,000
	Very salt	7,000–10,000
	Extremely salt	More than 10,000

* *Remarks:* The use for human consumption of subterranean water of higher salinity (up to 8,000 p.p.m.) without a noticeable harm to health has been recorded (Ward, 1946).

The stratification of fresh and salt waters as well as the occurrence of salt water above the water-bearing bed containing fresh water are not unusual phenomena (Makov, 1939).

In Pennsylvanian sands, for instance, fresh water often changes to brine within vertical range of 200–600 feet below the ground surface (Case, 1934).

As a matter of fact, the fresh and salt waters are in a permanent dynamic equilibrium: the gravitational-laminar motion of water along with the ionic diffusion process leads eventually to the accumulation of saline water and the formation of brines, particularly in the highly folded zones.

In the Volga River area, for example, the specific gravity of water which occurs in the Upper Carboniferous bed is 1·03; in the Lower Carboniferous formation 1·09; in the Upper Devonian rocks 1·16; in the Middle Devonian sediments 1·17, etc. (Ronov, 1945), while the specific gravity of sea-water is usually considered as equal to 1·025.

The salt water encroaching into the fresh water usually moves towards the general direction of the subsurface flow, being ellipsoidal in shape, but having been induced by heavy withdrawal, the salt water which accesses by lateral movement

has a shape of fingers or tongues. It is a fact that the fresh water moves (into a well, for example) more freely than the inflowing salt water.*

In the lowest part of the aquifer the salt water merges into the fresh water as a cone, and when the overlying fresh water is overpumped, this cone enters the well, contaminating the native fresh water (Fig. 9).

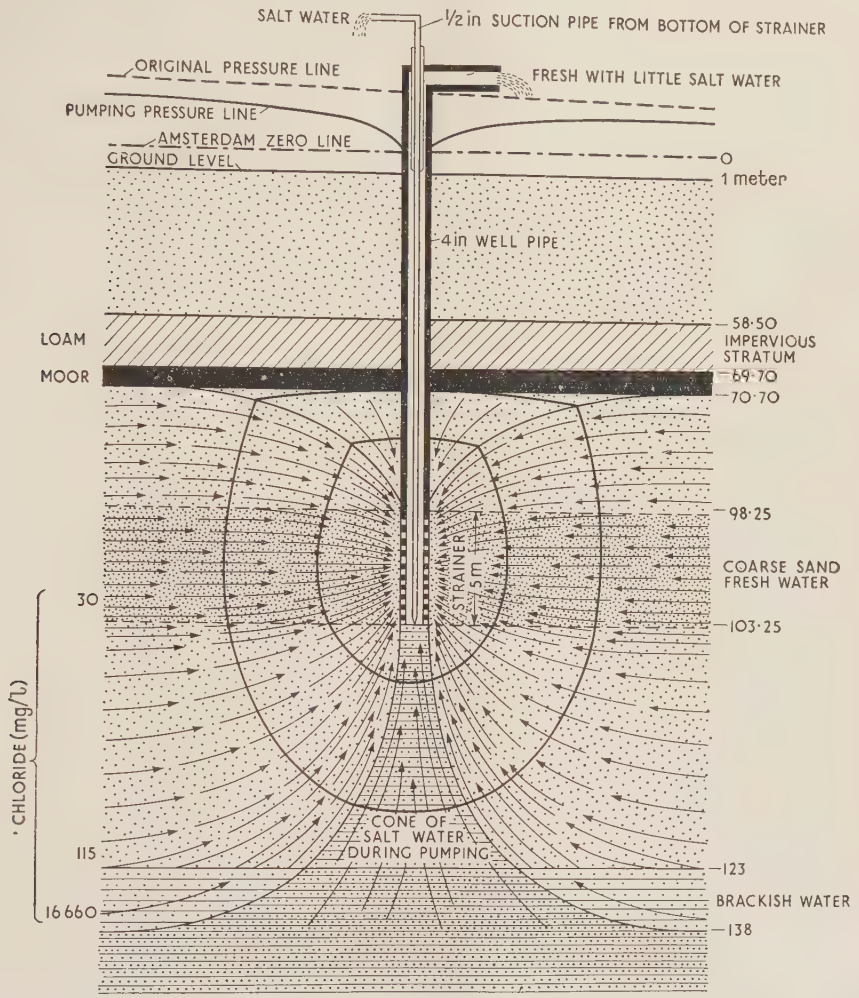

Fig. 9. The cone of salt water induced by pumping overlying fresh water (Penninк, 1905).

The water of higher salinity may or may not be under greater head, but as pumping is continued still longer the well discharges depreciated water indrawn from all the zones supplying the well.

The blend of fresh and salt water can also be determined by the natural change in the heads of underground waters of different salinity under the drawdown.

A decrease in hydraulic gradient slows down the velocity of flow, and this causes the increase in salinity concentration of underground water.

* I. I. Chebotarev: The salinity problem in the arid regions (January and February, 1955), *Water and Water Engineering*, London.

Table 13. *Change in the chemical composition of underground water due to the indraft of saline water from the underlying water-bearing bed* (Piper *et al.*, 1953)

Location of well	*Data of collection of water sample*	*Mode of reporting*	*Total salinity*	Na + K	Ca	Mg	Cl	SO_4	$HCO_3 + CO_3$	*Relative salinity*	*Type of water*
City of Newport Beach, well 4	Nov. 3rd, 1933	p.p.m.	338	24	49	14	40	15	196	1·0	Bicarbonate
		React. value %	100·0	11·2	26·5	12·3	7·1	1·9	41·0		
	June, 1934	p.p.m.	506	51	84	14	140	10	207	1·5	Bicarbonate-chloride
		React. value %	100·0	14·6	27·8	7·6	17·9	0·9	31·2		
	Aug. 30th, 1934	p.p.m.	818	87	145	27	342	10	207	2·4	Chloride-bicarbonate
		React. value %	100·0	14·3	27·4	8·3	28·8	0·6	20·6		
	Sept. 11th, 1934	p.p.m.	980	136	157	28	441	11	207	2·9	Chloride-bicarbonate
		React. value %	100·0	18·4	24·5	7·1	31·8	0·6	17·6		
	Sept. 4th, 1935	p.p.m.	1,261	102	273	45	675	0	166	3·7	Chloride
		React. value %	100·0	10·2	31·3	8·5	38·9	—	11·1		
	June 30th, 1935	p.p.m.	2,310	255	466	77	1,346	0	166	6·9	Chloride
		React. value %	100·0	14·8	26·7	8·5	33·7	0	6·3		

Remarks: The computation of reacting value in per cent has been done by the present author.

The interval 0·008–0·003 of the gradient corresponds with the visible change in salinity of water, as the motion of water in this case is rather slow, while the water is considered to be practically in stagnant conditions when the hydraulic gradient is as low as 0·0001 (Chebotarev, 1953; Shagoyanz, 1948).

The dynamic relationship of fresh to salt water during the pumping can be illustrated by the data presented in Table 13.

The data in Table 13 show that the hydraulic continuity which apparently exists in the underground water "system" in this case causes the indraft of salt water from beyond the area where the fresh water predominates and the store of the latter is inadequate to cover the capacity of the pump. This in turn results in the blend of fresh and salt water in a certain proportion, depending on the pressure-head, the hydraulic properties of the formation, etc.

The decrease in salinity of water with the time of pumping sometimes also occurs (Table 34), but such a change can take place only when the aquifer is strong enough to overcome the contamination of fresh water by salt water.

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Die häufigsten Elemente im Durchschnitt der Eruptivgesteine

H. Borchert
Mineralogisches Institut der Bergakademie, Clausthal

ABSTRACT

The average composition of eruptive rocks is best represented by the investigations of Sederholm, Vogt, and Grout. The figures of Clarke and Washington show too high values by far for Fe, Mg, Ca, Ti, Na, (and P), and too low values for Si and K. Also, in consequence of the composition of the sediments being not exactly known, the figures of F. E. Wickmann (1954) give too high parts of (juvenile) basaltic eruptives in comparison with the (palingenic) acid eruptive rocks.

Es ist allgemein bekannt und vielfach kritisiert (vgl. Rankama und Sahama, 1949), daß im Durchschnitt der Eruptivgesteine von F. W. Clarke und H.S. Washington (1924) ein zu großer Anteil basischer und nephelinreicher Gesteine enthalten ist; dadurch resultieren zu hohe, Werte für Fe, Mg, Ca, Na, Ti, und P und zu niedrige für Silicium und Kalium. Der wirkliche Durchschnitt der Eruptivgesteine ist aber eine so wichtige Bezugsgröße der Geochemie, daß die Bemühung um die besten Werte sinnvoll ist.

Nun liegen bereits drei Versuche vor, die tatsächlichen Anteile der verschiedenen Gesteine auf der Grundlage regional-geologischer Kartierung und gleichzeitiger Schätzung auch der räumlichen Anteile in der oberen Erdkruste zu erfassen. *Nur ein solches Vorgehen ergibt die Berechtigung, auch von Durchschnittsgehalten zu sprechen.* Das Gewicht dieser Untersuchungen von J. J. Sederholm (1925), J. H. L. Vogt (1931) und F. F. Grout (1938) erscheint hinreichend, um danach die wahren Durchschnittsgehalte der Eruptivgesteine zu korrigieren.

In der Tabelle 1 sind für die 9 häufigsten Elemente die Werte von Sederholm, Vogt, und Grout den bisher immer noch meist verwandten Werten von Clarke und Washington gegenüber gestellt. Die unabhängig voneinander gewonnenen Werte von Sederholm, Vogt, und Grout zeigen nun eine so weitgehende Übereinstimmung, daß eine Mittelung den Anspruch erheben darf, den wirklichen Durchschnittsgehalten der Gesteine zur Zeit am besten zu entsprechen. In Spalte 5 sind die entsprechenden Werte als Gewichts-% Element berechnet (wobei allerdings nicht in allen Fällen das rein arithmetrische Mittel gebildet worden ist und stets die zweiten Dezimalen vernachlässigt worden sind).

Ein wesentlicher Einwand gegen die Werte von Sederholm, Vogt, und Grout könnte sich darauf beziehen, daß in allen Fällen die Verhältnisse "alter Schilde" (Skandinavien, Finnland, Canada) die Grundlage der Mengenschätzungen geliefert haben. Gegenüber höheren Erdkrusten-Abschnitten—mit Ausnahme der obersten Teile, die wegen des basaltischen Vulkanismus wiederum zu hohe Anteile basischer Gesteine zeigen würden—könnte hieraus aber nur ein relativ zu großer Anteil an basischen Gesteine erwachsen. Tatsächlich dürften durch diese Ursache die Werte von Grout für Fe und Ti noch reichlich hoch liegen. Sederholm und Grout haben im übrigen auch die kristallinen Schiefer, Quarzite und

Tabelle 1

	(1) *Clarke*	(2) *Sederholm*	(3) *Vogt*	(4) *Grout*	(5) *Mittel S–V–G*	(6) *"Granit"*	(7) *"Basalt"*	(8) *Wickman*	(9) *Knopf*	(10) *Sedimente*
O	*46·4*	47·7	47·2	47·1	*47·3*	48·4	41·3	46·7	46·0	~46
Si	*27·6*	31·9	30·3	29·8	*30·3*	30·4	24·1	29·4	29·2	28·7
Al	*8·1*	7·8	8·2	8·9	*8·2*	8·1	7·9	8·0	8·4	9·5
Fe	*5·1*	3·6	$3·6_5$	4·0	*3·8*	2·9	8·9	4·8	4·6	5.8
Mg	*2·1*	1·0	1·5	1·1	*1·3*	0·8	4·0	1·9	1·8	1·4
Ca	*3·6*	2·5	3·1	2·9	*2·9*	2·3	7·2	3·8	3·7	0·4
Na	*2·8*	2·3	2·6	2·7	*2·6*	2·7	1·7	2·4	2·5	1·0
K	*2·6*	3·0	3·0	2·6	*2·8*	2·9	0·7	2·2	2·2	2·6
Ti	$0·6_3$	$0·2_5$	$0·3_3$	$0·4_9$	*0·4*	0·3	0·9	$0·4_8$	$0·4_4$	$0·6_5$

(1) Durchschnitt der Eruptivgesteine nach Clarke und Washington (1924).
(2) Durchschnitt aller Gesteine Finnlands nach J. J. Sederholm (1925).
(3) Durchschnitt der Eruptivgesteine nach J. H. L. Vogt (1931).
(4) Durchschnitt aller Gesteine des Canadischen Schildes nach F. F. Grout (1938).
(5) Mittel aus Werten von Sederholm, Vogt und Grout als "wahrer Durchschnitt der Eruptivgesteine."
(6) Durchschnitt der sauren Eruptivgesteine = "Granit" als Mischung von Daly's Granit und Granodiorit im Verhältnis 1 : 1 (Wickman 1954).
(7) Durchschnittliche Zusammensetzung von Plateau-Basalt ("Basalt") nach F. E. Wickman (1954).
(8) Durchschnittliche Zusammensetzung der Eruptivgesteine als Mischung von "Granit" und "Basalt" im Verhältnis 2, 13 : 1 nach F. E. Wickman (1954).
(9) Durchschnitt der Eruptiva der Cordilleren und Appalachen nach A. Knopf (1916).
(10) Durchschnittliche Zusammensetzung der Sedimente nach F. E. Wickman (1954).

Kalke in ihre Berechnungen einbezogen, sodaß ihre Werte bereits einen Gesamtdurchschnitt der Erdkruste repräsentieren. Es erscheint hierbei wichtig und charakteristisch, daß die Vogt' *schen Werte der reinen Eruptivgesteine* in der Regel zwischen den Zahlen von Sederholm und Grout rangieren; nur für Mg und Ca hat Vogt etwas höhere Werte erhalten. Alle Werte von Sederholm, Vogt, Grout und des daraus gewonnenen "Durchschnitts der Eruptivgesteine" bilden jedoch eine einheitliche Gruppe gegenüber den sicher "zu basischen" Werten von Clarke und Washington und der meisten Kompilatoren.

In neuester Zeit hat nun F. E. Wickman (1954) die Zusammensetzung des Durchschnitts der Eruptivgesteine aus geochemischen Bilanzen neu berechnet. Er kommt dabei zu dem Ergebnis, daß je cm^2 Erdoberfläche 194 ± 21 kg Eruptivgesteine im Laufe der Erdgeschichte in 209 ± 35 kg Sedimente zerfallen sind. Auch bei dem Anteil der verschiedenen Sedimente kommt F. E. Wickman zu recht ähnlichen Zahlen, wie sie H. Borchert (1951) bei einer geochemischen

Bilanz des Kohlenstoffs auf der Grundlage von Untersuchungen von C. W. Correns (1948) ermittelt hat.

Trotz dieser weitgehenden Übereinstimmung dürfte F. E. Wickman den Anteil der basischen Gesteine immer noch zo hoch bemessen. Wickman ermittelt zunächst den Durchschnittsgehalt der sauren Eruptivgesteine (="Granit"), indem die Daly's-chen Mittel von Granit und Granodiorit im Verhältnis 1 : 1 gemischt werden (Spalte 6 der Tabelle 1). Dann wird aus 11 Analysen verschiedener Basalt-Provinzen ein "durchschnittlicher Basalt" (Spalte 7) konstruiert. Weiterhin wird mit Gleichungs-Systemen für Al, Fe, Na und K untersucht, welches Mengenverhältnis von "Granit" zu "Basalt" am besten mit der Durchschnittszusammensetzung der Sedimente übereinstimmt. F. E. Wickman kommt zu dem Ergebnis, daß das Verhältnis "Granit": "Basalt" in den Grenzen 2·83 und 1·43 schwanken kann, wobei das Verhältnis "Granit" : "Basalt" = 2·13 : 1 als wahrscheinlichster Wert angenommen wird. Dieses "durchschnittliche Eruptivgestein" würde die Zusammensetzung von Spalte 8 haben. Es stimmt recht gut überein mit den Werten von A. Knopf (1916), die dieser aus der Erfassung der Eruptiva der nordamerikanischen Kordilleren und Appalachen gewonnen hat (Spalte 9).

Dennoch sollte diese Übereinstimmung nicht zu optimistisch beurteilt werden. Bei der Oberflächen-Kartierung dürfte der Anteil basaltischer Gesteine ein zu großes Gewicht bekommen haben, jedenfalls wenn man die wirklichen räumlichen Mengenanteile der Eruptiva in der Oberkruste erfassen will.

Grundsätzlich ist das Vorgehen von F. E. Wickman sicher in Ordnung. Auf alle Fälle ist die Mühe sinnvoll und lohnend zu ermitteln, mit welchen Anteilen einerseits der sauren, mit größter Wahrscheinlichkeit palingenen Eruptiva in der oberen Erdkruste wirklich zu rechnen ist, andererseits wie groß die Beteiligung der juvenilen basaltischen Eruptivgesteine ist (vgl. hierzu H. Borchert und E. Tröger, 1950). Aber der *Hauptunsicherheitsfaktor bei geochemischen Bilanzen ist immer noch die durchschnittliche Zusammensetzung der Sedimentgesteine.* Diese Sedimente sind von Wickman an Hand der Werte für "durchschnittlichen Schiefer," Roten Tiefseeton und Blauschlick m.E. mit zu hohen Werten z.B. für Fe und Ti angesetzt (Spalte 10). Ähnliches gilt auch für die Beurteilung der norwegischen Lehme durch den Altmeister der Geochemie V. M. Goldschmidt (1954, S.54). Dadurch wiederum müssen in den geochemischen Bilanzen die Eruptivgesteine "zu basisch" ausfallen. *Der Durchschnitt der Eruptivgesteine dürfte durch Spalte 5 derzeit am besten repräsentiert werden.* Das Verhältnis der sauren (palingenen) Eruptivgesteine zu den basaltischen (juvenilen) Eruptivgesteinen dürfte im Durchschnitt der oberen Erdkruste (rd. 16 km) bei etwa 4 : 1 liegen. Nach J. H. L. Vogt ergibt sich dies Verhältnis zu 3·7 bis 4·5.

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The normal distribution in geochemistry*

R. L. Miller
University of Chicago, Chicago 37, Illinois
and
Edward D. Goldberg
Scripps Institution of Oceanography, La Jolla, California

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ABSTRACT

The proposed geochemical law of Ahrens, that elements are distributed log-normally in igneous rocks, is critically examined. It is concluded that existing data do not confirm this proposition or suggest any extension of it. The application of statistics to geochemistry is formulated under the topics of (1) description of results and (2) statistical prediction. Meaningful interpretations of frequency distributions in nature are dependent upon a knowledge of the factors involved in the formation of the geological system under study, and a knowledge of the contribution of laboratory and field sampling errors to the numerical data.

Introduction

In the past year two stimulating papers (Ahrens, 1954a; Shaw and Bankier, 1954) have appeared in which the application of statistical methods to geochemistry are discussed.† In both of these papers the assumption of a normal distribution plays an important role. Frequency distributions of elements have been of primary importance in the consideration of geochemical abundances, and Ahrens (*loc. cit.*) has proposed a fundamental law of geochemistry: *the concentration of an element is log-normally distributed in a specific igneous rock.* He has suggested that this law may be extended by frequency distribution studies of other rock types. The purpose of the present investigation is to examine the proposition of Ahrens and to discuss the role of the normal distribution function for elements in nature. These propositions have recently been discussed in a limited sense by K. V. Aubrey (1954).

Discussion of Ahrens's Proposition

The published evidence for Ahrens's proposal consists of twenty frequency distributions of various elements in granites and diabases. A set of histograms were drawn in which the frequency distribution of a given element is displayed where the abscissa is divided into arbitrary intervals in units of p.p.m., and the ordinate gives the frequency of individual analyses whose results fall in a particular p.p.m. interval. This histogram is accompanied by a second in which the individual entries are the logs of the entries. The graphs purport to show that a log-transformation usually results in a normal distribution. Ahrens, on the basis of the above, then proposes his Fundamental Law of Geochemistry.

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† More recently Chayes (1954) has published a critical note on Ahrens's paper. Ahrens (1954b) has published a sequel to his original paper with further discussion in support of his earlier propositions. The present writers' work was completed independently and prior to the appearance of these two papers.

Visual examination of the graphs show that in many cases there is an undoubted tendency towards increase of symmetry of the histogram by using the log-transform. In other cases, however, no increase in symmetry or decrease in subsidiary peaks is visually apparent after use of the log-transform. The following points occurred to the writers:

(a) Histograms are often misleading. A slight change in the arbitrarily selected class interval may give an entirely different apparent shape to the histogram.

(b) Symmetry is not in itself a property solely possessed by the normal distribution.

(c) The sample sizes in every case small for purposes of determining the form of the frequency distribution. The sample sizes range from about 25 to 60. For example, if it is desired to test goodness of fit of a sample cumulative curve to a hypothetical curve whose parameters are specified in advance (in this case normal or log-normal), one procedure is to compute a percentage-error strip based on the theoretical curve. If the sample cumulative curve is outside this band at any point, the theoretical curve is rejected. The width of this band is determined in advance by the percentage-error one is willing to accept. The following figures, computed by the writers, illustrate sample sizes necessary for a given error band.

Interval or error band = 10 per cent.

Risk of being wrong by rejecting curve if outside of band	Minimum sample size required
0·01	1037 approx.
0·05	739 ,,
0·10	600 ,,

The reader interested in computing sample size required for other "error bands" at various levels of risk is referred to Dixon and Massey (1951, p. 257). Testing whether a sample comes from a normal distribution with parameters unspecified is more difficult, and minimum sample sizes would probably be still larger than the values given here.

In view of the preceding, the writers applied a simple graphical test to the data as given by Ahrens. The test involved plotting the cumulative frequencies on a special graph paper which is so designed that a normal or log-normal frequency distribution will plot as a straight line. The cumulative form of the frequency distribution has the advantage (for graphical analysis) of being independent of the arbitrary choice of class interval. Marked departure from a straight line indicates the distribution is not normal.*

The plots were made on the two kinds of paper for normal and log-normal

* The technique of testing goodness-of-fit by the use of Normal-Probability paper is described in detail in Dixon and Massey (1951) pp. 55-59. Normal and log-normal paper can be obtained from the Codex Book Co. Inc., Norwood, Mass. This test was used instead of Chi-square or Kolmogorov-Smirnov tests, (Miller, R. L., and Olson, E. R., in press), because of rapidity and ease in use.

distributions respectively. Due to the small sample sizes, the writers took the point of view that the test would not precisely indicate the existence of a normal or log-normal distribution, but would reliably show such cases where normal or log-normal were not correct inferences from the sample data. Table 1 gives the

Table 1

	Canadian granite	*Ontario diabase*	*New England granite*
Ga	*U**	?	
Sc	log-normal possible	arithmetic normal possible	
K	*U*	*U*	*U*
Rb		*U*	arithmetic normal possible
Co		*U*	
Zr	*U*	*U*	
V	log-normal possible	*U*	
La	*U*		
F	log-normal possible in Canadian and New England granites together.		
Ce	*U*		
Mo	log-normal possible in unnamed granites		
Pb	log-normal possible		
Cr	log-normal possible		

* *U* indicates neither a normal or log-normal distribution was found.

results of the graphic analysis of AHRENS's data. Six of the twenty sets of analyses are possibly log-normal, two of the twenty are possibly arithmetic-normal, and ten are neither log- nor arithmetic-normal. The remaining two are not in a form suitable for testing. We can only conclude that AHRENS's proposal is not justified by the data he presents.

Table 2 gives the results of further investigations by using the previously described graphic method on other published data, and on deep-sea sediment analyses of E. GOLDBERG and G. ARRHENIUS (unpublished). Again, the results do not confirm the proposed "Geochemical Law" or suggest any extensions of it.

APPLICATION OF STATISTICS TO GEOCHEMISTRY

In general terms, application of statistics to geochemistry may be formulated under two main topics: description, and statistical inference or prediction (e.g., CRÁMER and SHAW, *loc. cit.*).

Table 2. Further analyses of frequency distributions of elements in nature by use of normal and log-normal probability paper.

Element	*Reference*	*Result*
Cu in coal	Aubrey, 1954	possible log-normal
Zn in granites	Lundegårdh, 1949	*U**
Ca in Fe meteorites	Urey, 1953	possible log-normal
Na in Fe meteorites	do. do.	possible log-normal
Si in Fe meteorites	do. do.	*U*
Mg in Fe meteorites	do. do.	*U*
Al in Fe meteorites	do. do.	*U*
Ni in Fe meteorites	Goldberg *et al.*, 1951	*U*
Co in Fe meteorites	do. do.	*U*
Au in Fe meteorites	do. do.	*U*
Pd in Fe meteorites	do. do.	*U*
Ga in Fe meteorites	do. do.	*U*
Mg in glauconite	Hendricks and Ross, 1941	*U*
Ca in glauconite	do. do.	*U*
Na in glauconite	do. do.	*U*
K in glauconite	do. do.	*U*
Al_2O_3 in glauconite	do. do.	*U*
SiO_2 in glauconite	do. do.	*U*
Mno/NiO in pelagic sediments	Goldberg and Arrhenius (unpublished)	*U*
NiO in pelagic sediments	do. do.	*U*
MnO in pelagic sediments	do. do.	*U*
Ti in deep sea core 49BP	do. do.	possible arithmetic normal
K in deep sea core 49BP	do. do.	possible log-normal
Ti in deep sea core 50BP	do. do.	*U*
Mo in basalt and diabase	Kuroda and Sandell, 1954	*U*
Mo in intermediate rocks	do. do.	*U*
Mo in granite	do. do.	possible log-normal
Mo in silicic volcanics	do. do.	*U*
K_2O in granites (all granites in world analyzed between 1884-1913)	Washington, 1917	possible arithmetic normal

* *U* indicates neither a normal nor log-normal was found.

Description. Large sets of numbers, cumbersome and difficult to interpret, may be reduced to a useful form by the use of descriptive statistics. The average value, an expression of the degree of variation around the average and graphical representations of frequency distributions, are of obvious usefulness.

Statistical inference or prediction. Statistical inference goes beyond the problem of refining or condensing large masses of numerical data. Subjective inference, from a sample to a much larger collection from which the sample is drawn, is common and widespread. Statistical inference is a formalization of this procedure. For example, it is sometimes possible to state with preassigned confidence a range or interval which will include some parameter of a large collection (e.g., the mean) on the basis of a relatively small sample. This is legitimate, provided

the required mathematical assumptions are satisfied. These usually, but not always, involve, among others, the form of the frequency distribution.

The application of frequency distributions in statistical inference can be summarized in the following way:

A. The form of frequency distribution function of the fundamental set (total collection or statistical universe) is known, at least approximately.

1. If the frequency distribution is normal, a large number of statistical tests can be performed, many of them by use of tabulated functions.
2. If the frequency distribution is not normal but is of known form, a suitable transformation can often be made, so that the new set of values will be normally distributed. One may then proceed as above. For example, the logarithms of numerical results are sometimes normally distributed.

B. The frequency distribution function of the set is not known.

1. Non-parametric tests (distribution free methods) may be used for statistical inference, if the form of frequency function is not known, or one is not willing to assume its form.

The normal distribution has been emphasized in the development and application of mathematical statistics. This is due to both mathematical convenience and observational results. Many of the mathematical problems involved in the development of procedures for the utilization of statistical inference are greatly simplified if the unknown distribution is considered to be normal. Further, the central limit theorem, fundamental to mathematical statistics, states that under very general restrictions the sum of n independent variables is asymptotically normally distributed, whatever the distributions of the n independent variables may be. In several fields of science such as paleontology, biology, and physics, normal or asymptotically normal distributions have been found. In such studies the universes are often clearly defined (see below).

In geochemistry no models have yet been proposed to account for normal frequency distributions of chemical elements. The authors attempted to set up two types of models, and to test them against field or theoretical data. The first involved the Central Limit Theorem, in which a log-normal distribution arises under assumptions which appear plausible in a natural system (e.g., in which geological processes are at work). This schematization was first proposed by Crámer (1946, pp. 219-20). A second model was based on the "Law of Errors" interpretation of the normal distribution with regard to the influence of errors upon the field or laboratory techniques. The normal distribution was first described by Gauss and by Laplace. A derivation given in Levy and Roth (1936) is used by the writers (see Appendix A).

Both models failed to reflect natural situations that were conceived by the authors, although they appeared to be most flexible in their application. This of course does not mean that either model cannot work in a geochemical context.

An important consideration in this discussion is the concept of a statistical universe. In very general terms this involves a collection of objects which have in common some measurable property. The frequency distribution represents the way that various values of the measurable property are distributed within this universe.

Let us consider the phosphorus content of quartz samples, which constitute a collection of objects. It is first necessary to examine the limits of our "universe." Shall we consider both the high- and low-temperature quartz? Shall we confine the collection only to the North American continent? Shall we consider the phosphorous only included as apatite? Considerations of this sort should be made before any statistical analysis is attempted.

An illustration of the importance of the above can be found in such a simple procedure as comparing two sample averages. If the population variances are known (or even unknown) and are assumed equal, then a particular test is available. Following this mechanical procedure, one arrives at an answer which states, e.g., "sample results like the ones observed are probable if the two population means are equal, and improbable if they differ by more than a certain amount."

In the above case, it is clear that some knowledge or intuitive ideas of the population, in terms which are meaningful to the problem, should be available if clear interpretations of results are to be gained.

Unless such precautions are taken, there is a real danger of losing sight of the original problem by mechanically using formal and often complicated statistical procedures.

Conclusion

An alternative view to that held by Ahrens is advanced on the basis of the preceding considerations. It appears to the writers that the elements in geochemical universes are not all distributed as log-normal or as any other single function.* The complexities of the situation in terms of both chemical and geologic time concepts lead to the following proposition:

A more realistic expectation is that different population frequency distributions exist for separate groups of one or more elements with respect to various rock types or mineral suites. In particular, the distribution of an element in a single rock type may differ from the distribution of the same element in another rock type of some general classification such as igneous rocks. The frequency distribution of any element is postulated to be a function of the following interdependent factors:

1. Chemical environment of formation or deposition.
2. The nature and number of elements involved in the rock type or mineral suite.
3. Geologic time considerations.
4. The reversibility or irreversibility of the chemical reactions.

For example, one may consider the possibility that a particular element may have a characteristic frequency distribution in a certain rock type or mineral, but may change with time (e.g., diagenesis) from one rock type to another. An example of this is (a) nickel in siderite, vs. (b) nickel in pelagic sediments.

However, one should first consider the nature of the universe that is being

* In fact, it should be made clear that great difficulties are involved in showing that any set of empirical data is *precisely* described by a specific function. Thus the search for specific functions to describe universes in nature seems fruitless. On the other hand, if a universe is *approximately* described by a particular function, statements of prediction and comparison can be made. Herein lies the usefulness of such investigations! Even here it is possible that, for certain purposes, several functions will serve equally well.

sampled. Further, an evaluation of the *a priori* knowledge of the particular time-dependent chemical system is necessary before widespread sampling and analysis of frequency distributions is attempted. A major difficulty must be considered in a study of this sort. The numerical data are the result of two sets of factors, the first composed of laboratory and field sampling errors, the second of contributions by factors involved in the formation and stability of the particular rock type studied.* Unless the influence of these two sets of factors can be distinguished, the writers do not feel that meaningful interpretations of frequency distributions of elements in geochemical systems can be made.

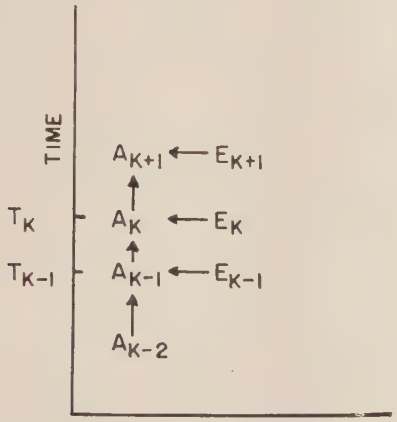

Fig. 1. Graphical representation of the CRÁMER model. E is an impulse acting upon A_k at time t_k. E_k is interpreted by the writers to be the total impulse composed of all the forces operating on A_k at time t_k.

We thus doubt the value of a statistical examination of empirical data in the absence of a meaningful hypothesis, and with no attempt to define the universe or universes which are being sampled. We believe that in such cases a model or analogue should be erected, drawing from both theory and known field relationships for its construction. In this context, statistics would be useful in testing those parts of the model where the parameters are unknown, but empirical data are available.

APPENDIX A

The following arguments paraphrase CRÁMER's discussion. Consider an individual measure A such as the amount of a chemical element in given rock (e.g., zirconium in a diabase). This measure A takes on various values over a time sequence t_0 to t_N. The CRÁMER model is schematically pictured in Fig. 1. The E_k are considered to be "independent random variables," and it can be seen above that the value of A at time t_k is the result of the total impulse E_k and the value of A at the previous time $t_k - 1$. The following equation states the situation:

$$A_{k+1} = A_K + E_{k+1}\, G(A_k)$$

where $G(A_k)$ is some function of the value of A at previous time t_k.

* For example, there is considerable published work on experiments designed specifically to evaluate errors of measurement (i.e., evaluation of results and design of procedure by analysis-of-variance techniques). The way the field samples are collected and handled is also of primary importance in a study of this sort. There is available an extensive literature on statistical sampling techniques, some of which may be reasonably adapted to the field-sampling aspects of the problem. YOUDEN (1951) from a chemical point of view, COCHRAN (1953) for sampling, and KRUMBEIN and MILLER (1953) for a summary of work in geology, are suggested, for further reading.

The successive values of A are thus put into cumulative form as illustrated by Fig. 2, where

$$A_{k+1} - A_k = E_{k+1}\, G(A_k)$$

and

$$E_1 + E_2 + \ldots + E_n = \sum_{0}^{n-1} \frac{A_{k+1} - A_k}{G(A_k)}$$

If the E_i's are small and n is very large,

$$E_1 + E_2 + \ldots + E_n = \int_{A_0}^{A} \frac{dt}{G(t)}.$$

The Central Limit Theorem (Crámer, 1946, p. 214) states (with mathematical conditions satisfied) that whatever the distribution of the independent variables E_i, the sum

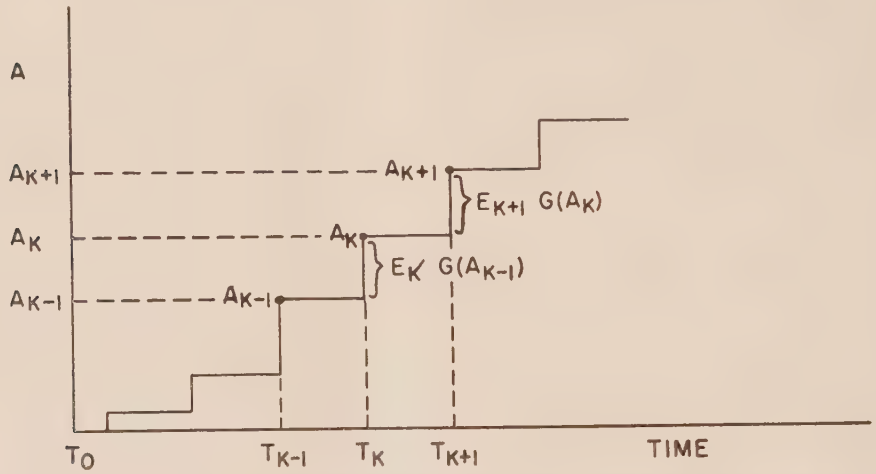

Fig. 2. The values of A as a function of time as influenced by the impulses E_i.

$E = E_1 + E_2 + E_3 + \ldots + E_n$, is asymptotically normal. Crámer in his model has thus developed the relation $E = \int_{A_0}^{A} \frac{dt}{G(t)}$, and states that the various values of this integral are normally distributed.

If $G(t) = t$ (the effect of each impulse directly proportional to A_k), then $\int_{A_0}^{A} \frac{dt}{G(t)}$ becomes $\int_{A_0}^{A} \frac{dt}{t}$, and $\log A$ is normally distributed, giving a log-normal distribution, the form referred to by Ahrens.

The mathematical assumptions are: (a) E_n and E_i are independent random variables; (b) their number is large and the effect of any one is small; (c) the mean and standard deviation are finite; and (d) the third moment about the mean exists.

Several possibilities for utilizing such a model as a reasonable explanation of the normal or log-normal distribution of elements in nature are discussed below.

The difficulties in the prediction of element distributions in a particular set or universe become evident upon examination of the processes that give rise to a set or universe consideration. Let us consider a major geological process, accumulation of deep-sea sediments. The chemical composition of the oceans is fairly uniform.

In the formation of a pelagic sediment we are concerned both with the genetic components originally building up the deposits, and with changes taking place after deposition. We shall concern ourselves solely with the former process. Here, each addition of a component may be considered as an impulse E_k. As an example, the nickel of pelagic clays probably arises from

two sources, the lithosphere and precipitation processes in the ocean (Goldberg, 1954). Although the frequency distribution of nickel in the hydrogenous component (manganese oxides) and in the lithogenous component (including pyroclastics) may each be normally distributed, a mixture of the two as found in nature may not be. The observed frequency distribution of nickel in pelagic sediments is not normal, and may reflect the above hypothesis.

Crámer states that the sequency of impulses, $E_1 \ldots, E_n$, are to be considered random variables. Thus the probability that any impulse E_n takes on a certain value (has a certain directed effect in our context) is not in any way influenced by the values assumed by the previous $n-1$ impulses. Therefore, the distribution of the random variable E_n is independent of any hypothesis made with respect to the value assumed by the combined variable $(E_1 \ldots E_{n-1})$, so that E_n and $(E_1 \ldots E_{n-1})$ are independent.* In the case of the pelagic sediments, an example of a meaningful set of E_i's would be that of total environmental effect on element A at various instants in time, during deposition and also after deposition right up to the time the deposit is analyzed. In our context, the total environment previous to time E_n thus should have no effect on the value taken by E_n. This requirement of independence does not seem to satisfy the situation as it exists in nature.

It is not our purpose, however, to discuss the merits of the model described above, but to illustrate how the use of the Central Limit Theorem in a model may lead to a reasonable expectation of the normal or log-normal distribution for an element.

A derivation of the normal distribution which is not dependent on the Central Limit Theorem is given in Levy and Roth (1936), pp. 118–120; see also Lindsay (1941), p. 35, and Lindsay and Margenau (1936), pp. 181-187. In this case it is required to visualize a natural situation where a variable x (such as amount of an element in p.p.m.), varies about a mean value a in such a way that the individual variations are independent of one another. The most frequent value corresponds to the average value, and the range of values of the deviations is $-\infty$ to $+\infty$. The infinite range is obviously impossible for an element in p.p.m., but is introduced for mathematical simplicity (see, for example, Lindsay (1941), p. 35).

The assumptions include;

(1) The deviations $\xi_i = (x_i - a)$ are independent of one another;
(2) P, a function of $\xi_1 \xi_2 \ldots \xi_n$ and of a, is continuous and differentiable over the entire range (which is from $-\infty$ to ∞);
(3) There is a single greatest value of P in the range of the variable;
(4) The value of a which makes P a maximum is the average value.

The above-mentioned derivation and the assumptions which underlie it seem to the writers to best fit a situation in geochemistry where experimental errors form a distribution about some "true" analytical value.

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* Crámer (1946), p. 161.

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Radioactive equilibrium in ancient marine sediments*

Irving A. Breger
U.S. Geological Survey, Washington 25, D.C.

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ABSTRACT

Radioactive equilibrium in eight marine sedimentary formations has been studied by means of direct determinations of uranium, radium, and thorium. Alpha-particle counting has also been carried out in order to cross-calibrate thick-source counting techniques. The maximum deviation from radioactive equilibrium that has been noted is 11 per cent—indicating that there is probably equilibrium in all the formations analyzed. Thick-source alpha-particle counting by means of a proportional counter or an ionization chamber leads to high results when the samples contain less than about 10 p.p.m. of uranium. For samples having a higher content of uranium the results are in excellent agreement with each other and with those obtained by direct analytical techniques. The thorium contents that have been obtained correspond well to the average values reported in the literature. The uranium content of marine sediments may be appreciably higher than the average values that have been reported for sedimentary rocks. Data show that there is up to fourteen times the percentage of uranium as of thorium in the formations studied, and that the percentage of thorium never exceeds that of uranium. While the proximity of a depositional environment to a land mass may influence the concentration of uranium in a marine sediment, this is not true with thorium.

Introduction

Alpha- and beta-particle counting methods have been applied to selected marine sediments to determine if radioactivity might have served as the source of energy for the conversion of complex organic substances into crude oil (Whitehead, 1950; Burton and Sullivan, 1951; and Breger and Whitehead, 1952). In these investigations, as in other work on the radioactivity of sedimentary rocks (Bell, Goodman, and Whitehead, 1940; Evans and Goodman, 1941; Beers and Goodman, 1944; Russell, 1944; and Beers, 1945), it has been assumed that the various members of both the uranium and thorium series were in secular equilibrium.

To investigate radioactive equilibrum in a number of marine sedimentary formations that had previously been studied in detail (Burton and Sullivan, 1951), composite samples were prepared for the direct determination of uranium, radium, and thorium. Alpha-particle counting was also carried out on the composites in order to cross-calibrate thick-source counting techniques.

Samples

Cretaceous from eastern Texas

Samples from the Upper Cretaceous rocks of eastern Texas, representing the Austin chalk, Eagle Ford shale, and Woodbine sand, along with their constituent members, were supplied by the Humble Oil Co.

Austin chalk—This composite was made up from 6 g each of 16 samples taken from 4 wells: No. 1 L. A. Bryan Estate, Wood County, Tex.; No. 1 D. C. Irons, Upshur County, Tex.; No. 1 L. L. Plantation, Anderson County, Tex.; and No. 1 E. E. Birdwell, Anderson County, Tex.

Eagle Ford shale—6 g each were taken from 26 samples from the above 4 wells.

Woodbine sand—5 g were taken from each of 30 samples from the above 4 wells.

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Cretaceous of Mississippi

Samples from the Upper Cretaceous rocks of Mississippi were made available for this work by the Gulf Oil Co. The following formations correspond, respectively, to the Austin, Eagle Ford, and Woodbine in eastern Texas.

Selma chalk—Using 33 samples from 2 cores, 2·5 g were taken from each sample and mixed to prepare the composite. The wells represented are Mrs. L. T. Simpson No. 1, Baxterville field, Miss., and Berry No. 1, Gwinville field, Miss.

Lower part of Eutaw formation—Using 24 samples from the above 2 cores, 2·5 g were taken from each sample.

Tuscaloosa formation—Using 55 samples from the same 2 cores as above, 2·5 g were taken from each for the preparation of the composite.

Nodular shale of Miocene age, California

Using 135 samples from 9 core sections from the Lawndale field, Calif., ranging in depth from 8090 to 8237 ft, 0·5 g of material were taken from each to make up a composite. These core sections were obtained from Seaboard Community Well No. 6-1 through the courtesy of the Standard Oil Co. of Calif.

Geological and chemical evidence (HOOTS, BLOUNT, and JONES, 1935) supports the contention that this shale is the most likely source bed for the oil in the basal Miocene conglomerate and schist in the Playa del Rey and other nearby fields.

Antrim shale, Michigan

A specimen of Antrim shale from the geological collection of the Massachusetts Institute of Technology was used. Approximately 200 g of this material were ground and mixed to provide a sample for analysis. The Antrim shale of Late Devonian age has been considered a possible source bed for the crude oil in Osceola County, Mich. (SHEPPARD and WHITEHEAD, 1946).

EXPERIMENTAL DATA

Determination of uranium

The extraction-fluorimetric technique of GRIMALDI, MAY, and FLETCHER (1952) was employed using duplicate samples and highly purified reagents. Results are shown in Table 1.

Table 1. *Uranium contents and calculated radium equivalents*

Formation	*Uranium content**			*Calculated radium equivalent of uranium*	
	No. of analyses	*p.p.m.*	*Standard deviation p.p.m.*	($\times 10^{12}$ *g/g*)	*Standard deviation* ($\times 10^{12}$ *g/g*)
Austin chalk	2	2·80	0·09	1·01	0·03
Selma chalk	2	3·08	0·22	1·11	0·08
Woodbine sand	2	1·66	0·04	0·60	0·01
Tuscaloosa formation	2	2·81	0·16	1·02	0·06
Eagle Ford shale	2	2·25	0·01	0·81	0·01
Lower part of Eutaw formation	2	2·53	0·05	0·92	0·02
Nodular shale of Miocene age	2	14·4	0·30	5·21	0·11
Antrim shale	2	17·5	0·40	6·34	0·14

* Analysts: F. S. GRIMALDI and E. BRITTIN, U.S. Geological Survey.

Determination of radium

Analyses were carried out by fusing 0·5- to 0·6-g samples in the direct-fusion vacuum furnace described by Evans (1935) and Goodman and Evans (1941). Before analysis the empty graphite crucible was evacuated, raised to fusion temperature, saturated with dry nitrogen to displace air from its pores, and cooled. The sample was then fused *in vacuo* for 40 min, and the radon so liberated was flushed by a current of dry nitrogen through a magnesium perchlorate drying tube into an ionization chamber. Sandstone samples were mixed with five parts by weight of sodium carbonate to assure complete fusion and release of radon. After allowing 3 h for the radon to reach equilibrium in the chamber, counting was carried our with the ion-collecting voltage set at 135 V and using a vibrating-reed electrometer. Alpha-particle pulses were recorded on a strip chart for 3 to 10 h, depending upon the amount of radon present. Correcting for background, for the decay of radon, and using an instrumental calibration constant based upon the analysis of a standard, the radium content of the sample was calculated. Radium determinations are shown in Table 2.

Table 2. Radium- and radon-loss determinations

Formation	*Radium*			*Radium equivalent of radon loss*		
	No. of analyses	($\times 10^{12}$ *g/g*)	*Standard deviation* ($\times 10^{12}$ *g/g*)	*No. of analyses*	($\times 10^{12}$ *g/g*)	*Standard deviation* ($\times 10^{12}$ *g/g*)
Austin chalk	2	0·97	0·10	2	0·15	0·02
Selma chalk	2	0·94	0·08	1	0·20	—
Woodbine sand	3	0·50	0·05	2	0·09	0·00
Tuscaloosa formation	2	0·83	0·00	–	—	—
Eagle Ford shale	2	0·65	0·01	3	0·15	0·03
Lower part of Eutaw formation	2	0·77	0·04	3	0·13	0·01
Nodular shale of Miocene age	2	3·96	0·10	2	1·15	0·04
Antrim Shale	2	5·15	0·27	1	1·81	—

Determination of radon loss

Some radon is lost from the surface of sample particles during evacuation prior to fusion in the vacuum furnace. To determine this quantity of radon, which has been termed radon loss, 25- to 30-g samples were placed in 200-ml bottles, which were then evacuated. Following replacement of the air with dry nitrogen at atmospheric pressure, the samples were stored for 5 to 30 days. After recording the exact period of storage, the nitrogen and radon were pumped into the ionization chamber described above, and the radon was calculated as equivalent grams of radium per gram of sample. Radium equivalents of radon loss are shown in Table 2.

Determination of thorium

The following procedure, adapted from the methods of Urry (1935), and Goodman and Evans (1941), was used to determine the thorium content of five of the eight formations under consideration.

10 g of sample were thoroughly mixed with 30 g of sodium carbonate and 1 g of barium chloride. The mixture was then fused for 2 h in a nickel or platinum crucible. After fusion the crucible was quenched and its contents ground to a fine powder and dissolved in 200 ml of doubly distilled water. After the solution had been allowed to stand for several days it was filtered on a 120-mm Buchner funnel, and the precipitate was washed with 200 to 400 ml of

saturated sodium carbonate solution. The mean time of the filtration was recorded, as this step marked the separation of radiothorium from thorium X.

The filtrate containing the radiothorium (Th^{228}, half-life 1·90 years) was rejected. The precipitate containing the thorium X (Em^{224}, half-life 3·64 days) was washed into a beaker with 10 ml of dilute hydrochloric acid. The filter paper was removed, 90 ml of concentrated hydrochloric acid was added, and the solution was evaporated to dryness on a hot plate to dehydrate the silica. The residue was dissolved in 100 ml of concentrated nitric acid and was taken to dryness on the hot plate in order to oxidize iron salts to ferric oxide. The residue was then dissolved in approximately 50 ml of 1- to 2-*N* nitric acid and filtered. The filtrate was finally adjusted to a volume of 50 ml and poured into a round-bottom flask for measurement of thoron. Thoron (half-life 54·5 sec) was flushed from the solution by a slow stream of nitrogen, which was then passed through a heated ionization chamber with the ion-collecting voltage at 45 V. Recording was carried out as described for radon. As in the case of radon measurements, the apparatus was calibrated by means of standard samples. Thorium analyses are shown in Table 3.

Table 3. Thorium analyses

Formation	*Thorium*		*Radium equivalent of thorium*
	No. of analyses	*p.p.m.*	($\times 10^{12}$ *g/g*)
Austin chalk	1	2·8	0·29
Selma chalk	1	2·0	0·21
Tuscaloosa formation	1	0·2	0·02
Nodular shale of Miocene age	1	3·6	0·38
Antrim shale	1	2·8	0·29

Table 4. Radium equivalents of thick-source alpha-particle counting

Formation	*Proportional counting*			*Ionization-chamber counting*		
	No. of determinations	($\times 10^{12}$ *g Ra/g*)	*Standard deviation* ($\times 10^{12}$ *g Ra/g*)	*No. of determinations*	($\times 10^{12}$ *g Ra/g*)	*Standard deviation* ($\times 10^{12}$ *g Ra/g*)
Austin chalk	4	1·61	0·25	5	2·13	0·35
Selma chalk	4	2·28	0·07	–	—	—
Woodbine sand	4	2·10	0·10	7	3·29	0·65
Tuscaloosa formation	2	2·91	0·01	–	—	—
Eagle Ford shale	4	2·58	0·10	6	3·33	0·45
Lower part of Eutaw formation	3	2·25	0·11	3	3·56	0·20
Nodular shale of Miocene age	3	5·41	0·19	2	5·07	0·25
Antrim shale	1*	7·12	—	–	—	—

* Single run, 16·7 hours in duration.

Proportional alpha-particle counting

A low-background, commercially available proportional alpha-particle counter was used in this work. The bell-type counting chamber was large enough to accommodate a thick source having an area of 25 cm^2. Multiple 2-hour runs were carried out with seven of the eight samples to obtain the desired degree of accuracy. Radium equivalents of these thick-source counts are shown in Table 4.

Ionization-chamber alpha-particle counting

The ionization chamber described by Nogami and Hurley (1948) was used. Pulse amplification was effected by means of a vibrating-reed electrometer, and pulses were recorded by a strip-chart potentiometer. Samples with areas of 80 cm^2 were used to obtain records that could be conveniently counted. An ion-collecting potential of 135 V was applied to the chamber, and counting was carried out for periods of 2 to 6 h. Perhaps as a result of the introduction of air, inconsistently high results were usually recorded during the first 2 h following the placing of a sample in the ionization chamber. For this reason counting was started after a sample had been in position in the chamber for a minimum of 2 h. Radium equivalents for the data obtained with the ionization chamber are shown in Table 4.

Calculations

The radium equivalents of uranium that are shown in Table 1 were obtained using the following half-lives calculated from the data of Hollander, Perlman, and Seaborg (1953) and assuming secular equilibrium:

$$U^{238}\ t_{1/2} = 4{\cdot}49 \times 10^9 \text{ years}$$

$$Ra^{226}\ t_{1/2} = 1{\cdot}622 \times 10^3 \text{ years}$$

Radium equivalents for thick-source alpha-particle counting (Table 4) were calculated from Bragg-Kleeman absorption factors (Bragg and Kleeman, 1905) and the formula given by Nogami and Hurley (1948). The composition of sericite was chosen as an approximation of the average composition of the unknown inorganic constituents of the formations. The Woodbine sand was considered to be relatively pure quartz. The values calculated for organic contents are based on the organic carbon contents given by Burton and Sullivan (1951) for all the formations but the Antrim shale. The organic content of the Antrim shale has been estimated from data given by Beers (1945). Minor variations in the approximations result in no serious errors in the calculation of radium equivalents, as the absorption factors for most minerals likely to be present in these sedimentary formations vary only from about $1{\cdot}47 \times 10^{-3}$ g/cm^3 to $1{\cdot}54 \times 10^{-3}$ g/cm^3 (Nogami and Hurley, 1948). The calculated absorption factors are listed in Table 5. Radium equivalents for thorium (Table 3) were similarly calculated, using the thick-source alpha-particle radium equivalent (Nogami and Hurley, 1948).

The criterion for radioactive equilibrium in the uranium series rests in the comparison of the radium theoretically equivalent to the uranium in the formations with the radium actually present in the samples. The radium actually present is equivalent to that found by direct determination, using the vacuum furnace plus that represented by the radon loss, which is separately measured. Ratios of actual to theoretical radium content are shown in Table 6.

Table 5. Absorption factors for calculating equivalent radium contents from thick-source alpha-particle counts

Formation	*Assumed composition*		*Absorption factor* (μd) ($\times 10^3$ g/cm^3)
	Components	*Per cent*	
Austin chalk	Calcium carbonate	88	
	Sericite	10	1·54
	Organic matter	2	
Selma chalk	Calcium carbonate	88	
	Sericite	10	1·54
	Organic matter	2	
Woodbine sand	Quartz	98·75	
	Organic matter	1·25	1·47
Tuscaloosa formation	Sericite	98·75	
	Organic matter	1·25	1·52
Eagle Ford shale	Sericite	98·75	
	Organic matter	1·25	1·52
Lower part of Eutaw formation	Sericite	98·75	
	Organic matter	1·25	1·52
Nodular shale of Miocene age	Sericite	92·75	
	Organic matter	7·25	1·48
Antrim shale	Sericite	92·75	
	Organic matter	7·25	1·48

Table 6. Radioactive equilibrium in the uranium series

Formation	*Theoretical radium*		*Actual radium*		*Ratio: Actual radium/ theoretical radium*	
	Radium equivalent of uranium ($\times 10^{12}$ g/g)	*Standard deviation* ($\times 10^{12}$ g/g)	*Direct detn. of radium plus radium equivalent of radon loss* ($\times 10^{12}$ g/g)	*Standard deviation* ($\times 10^{12}$ g/g)	*Ratio*	*Standard deviation*
Austin chalk	1·01	0·03	1·12	0·10	1·11	0·09
Selma chalk	1·11	0·08	1·14	0·11	1·03	0·12
Woodbine sand	0·60	0·01	0·59	0·05	0·98	0·09
Tuscaloosa formation	1·02	0·06	—	—	—	—
Eagle Ford shale	0·81	0·01	0·90	0·03	1·11	0·04
Lower part of Eutaw formation	0·92	0·02	0·90	0·04	0·98	0·05
Nodular shale of Miocene age	5·21	0·11	5·11	0·11	0·98	0·03
Antrim shale	6·34	0·14	6·96	0·27	1·10	0·04

Radium equivalents obtained by alpha-particle counting should total those from both the uranium and thorium series. Unfortunately, these studies had to be terminated before the completion of the thorium analyses; nevertheless, it is possible to draw some conclusions from the data obtained. In Table 7, ratios are shown for seven formations. These ratios are for calculated totals of radium-plus-thorium equivalents to the radium equivalents calculated from alpha-particle counts. In order to compare the proportional and ionization-chamber counting techniques in the absence of sufficient data for thorium, ratios have also been calculated without the values for thorium. Data from Table 4 have been used in establishing these ratios.

Table 7. *Ratio of radium determined experimentally to radium equivalents calculated from alpha-particle counts*

Formation	*Radium plus radium equiv. of thorium* ($\times 10^{12}$ *g/g*)	*Ratio: Total radium*/thorium plus radium equiv.*		*Ratio: Total radium*/radium equiv.*	
		Proportional counter	*Ionization chamber*	*Proportional counter*	*Ionization chamber*
Austin chalk	1·41	0·88	0·64	0·70	0·51
Selma chalk	1·35	0·59	—	0·50	—
Woodbine sand	—	—	—	0·29	0·18
Eagle Ford shale	—	—	—	0·35	0·27
Lower part of Eutaw formation	—	—	—	0·40	0·25
Nodular shale of Miocene age	5·49	1·01	1·08	0·95	1·01
Antrim shale	7·25	1·02	—	0·98	—

* Total radium equals radium determined directly plus radium equivalent of radon loss.

Discussion and Conclusions

Evans and Goodman (1941) reported the average uranium content of limestones to be about 1·3 p.p.m. and of other sedimentary rocks to be about 1·2 p.p.m. These data have been quoted (Rankama and Sahama, 1950) as bases for comparison. In this work the uranium contents of the Austin and Selma chalks have been found to be about 3 p.p.m., a figure somewhat higher than that given by Evans and Goodman (1941) for limestones. For two shales and two sandstones the average uranium content has been found to be about 2·3 p.p.m.; two other shales, the nodular shale of Miocene age of California and the Antrim shale, contain, respectively, 14·4 and 17·5 p.p.m. of uranium. It would appear from these data that the uranium content of marine sediments may be appreciably higher than the average values given by Evans and Goodman (1941).

From Table 7 it is apparent that thick-source alpha-particle counting, using a proportional-type counter or an ionization chamber, leads to high results for those samples that contain less than about 10 p.p.m. of uranium. Moreover, use of the

ionization chamber results in higher values than are obtained with a proportional counter, and also results in a lower degree of reproducibility of results. When samples containing 14 p.p.m. or more of uranium were measured, thick-source alpha-particle counting by either technique yielded results in excellent agreement with those obtained by direct analytical techniques. To account for the discrepancies noted with samples containing less than 14 p.p.m. of uranium, it has been suggested by Senftle (personal communication) that the failure to sweep thoron completely from either counter might result in the production of inordinately high alpha-particle counts. If thoron is a major factor, then it should be possible to eliminate this source of error by more thorough sweeping of thoron from the counters during measurements. Using the following formula to establish the rate

Table 8. Relationship of rate of sweeping of ionization chamber to per cent of thoron remaining in chamber*

Sweeping rate cm^3/sec	*Thoron remaining*† *per cent*
1	100
10	91
20	67
50	38
100	21
500	5
1000	0

* Assumed volume = 2000 cm^3.
† Based on complete release of thoron from particle grains at time of formation.

at which sweeping of the ionization chamber must be carried out to eliminate the contribution from thoron, the data of Table 8 have been obtained.

Percentage of total thoron formed that decays in chamber $= [1 - e^{-\lambda(V/v)}]100$

$\lambda =$ decay constant for thoron.
$V =$ volume of ionization chamber in cm^3.
$v =$ gas-flow through chamber in cm^3/sec.

These data show that for an ionization chamber having a volume of 2000 cm^3—approximately the volume of the chamber used in this work—it is necessary to flush the chamber with as much at 100 cm^3 of gas per second in order to remove 80 per cent of the contribution from thoron. This is based on the assumption that there is complete release of thoron at the time of formation from sample particles. Sweeping at lower rates will result in high alpha-particle counting rates as a consequence of the contribution from thoron. Therefore, in those samples in which the thoron content is of the same order of magnitude as the uranium content, the contribution from thoron may be so appreciable, if rapid sweeping of the chamber is not carried out, that it results in high alpha-particle counts. As the ratio of uranium to thorium increases, the contribution to the alpha-particle

count from thoron should decrease. Therefore, alpha-particle counting of samples containing less than approximately 10 p.p.m. of uranium apparently must be carried out while gas flows rapidly through the counting chamber. Unless this precaution is taken, thick-source alpha-particle counts will be too high.

The thorium contents of the five marine sediments that were analyzed in this work ranged from $0{\cdot}2 \times 10^{-6}$ to $3{\cdot}6 \times 10^{-6}$ g/g with an average of $2{\cdot}3 \times 10^{-6}$ g/g. This average corresponds well with the value of $3{\cdot}3 \pm 0{\cdot}7 \times 10^{-6}$ g/g of thorium given by Evans and Goodman (1941) for sedimentary rocks, and with the value of about 5×10^{-6} g/g of thorium in marine red clay given by Picciotto and Wilgain (1954). Koczy has suggested that his value of $0{\cdot}1 \times 10^{-6}$ g/g of thorium in marine red clay may be low as a result of incomplete extraction of thorium from the clay prior to analysis (Koczy, 1949a; and in Picciotto and Wilgain, 1954).

Ratios of uranium to thorium for five of the formations for which sufficient data are available (Table 9) show that there is as much as fourteen times the percentage of uranium as thorium in these marine sediments. Although the percentages of thorium and uranium are equal in the Austin chalk, in no formation does the percentage of thorium exceed that of uranium.

Table 9. Uranium-thorium ratios

Formation	*Uranium p.p.m.*	*Thorium p.p.m.*	*Uranium/thorium*
Austin chalk	2·80	2·8	1·0
Selma chalk	3·08	2·0	1·5
Tuscaloosa formation	2·81	0·2	14·1
Nodular shale of Miocene age	14·4	3·6	4·0
Antrim shale	17·5	2·8	6·3

Recent estimates indicate the average uranium content of sea-water to be approximately 1·1 to 2·4 micrograms per litre (Koczy, 1950; and Stewart and Bentley, 1954). The average thorium content of sea-water has been reported to be about 0·7 microgram per litre (Masayoshi and Azuma, 1949). The thorium content of marine sediments is approximately one thousand times that in sea-water and is very constant. While the minimum concentration factor for uranium is also about 1000, this factor is not constant, but may be dependent upon unusually high concentrations of uranium in sea-water. Where the percentage of uranium in a restricted marine environment may be high, as a consequence of the influx of the element from surrounding formations, the uranium content of the marine sediment apparently rises. The existence of such a set of conditions apparently led to the concentration of uranium in the Cambrian alum shale of Sweden (Koczy, 1949b). The thorium content of the alum shale is low ($0{\cdot}6 \times 10^{-6}$ to $1{\cdot}9 \times 10^{-6}$ g/g) and, as has been found for other marine sediments, does not vary widely as does the concentration of uranium. The low and consistent percentages of thorium in marine sediments taken from deep or shallow seas (Koczy, 1949a; and Picciotto and Wilgain, 1954) indicate that the concentration of the

thorium is not influenced by proximity of the depositional environment to a land mass.

The primary objective of this work was to establish the status of equilibrium of the uranium series for a suite of marine sedimentary rocks. As is indicated in Table 6, the ratio of radium found to the radium equivalent of the uranium in the composites is in each case practically unity. The maximum deviation from equilibrium conditions that has been noted is 11 per cent; the maximum standard deviation of a suite of measurements is 12 per cent. From the data, it would appear, therefore, that there is probably radioactive equilibrium in all of the formations that have been analyzed.

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The uranium geochemistry of Lassen Volcanic National Park, California

J. A. S. Adams
Department of Geology, The Rice Institute, Houston, Texas

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ABSTRACT

The uranium contents and relative alpha-particle activities have been determined on thirty-nine samples from Lassen Volcanic National Park. Sodium and potassium were also determined on nineteen of the samples. Secular radioactive equilibrium to within sampling and analytical error was found between the uranium values and the radium values of other workers. The K_2O/U ratio was found to be constant over a fourfold variation in uranium. The relative alpha-particle activity to uranium ratio was also found to be constant in the main Lassen sequence. There is some evidence that zircon crystals contain a proportion of the uranium in the Lassen volcanic rocks.

Introduction

It has long been known that the more silicic rocks are more radioactive and more uraniferous than the less silicic rocks (Strutt, 1905). This generalization was firmly established by many later researches, particularly by the work of Evans and Goodman (1941), who also summarized and evaluated earlier radiometric data on rocks. Still more recent studies (Senftle and Keevil, 1947; Davis and Hess, 1949; and others) added more confirmation. Most of the recent studies used the technique of direct-fusion for releasing radon from the rock sample. The alpha-particle activity of the radon was then measured, and that quantity was used to calculate the equilibrium amounts of radium and uranium. The details of technique, the assumptions, and the estimated errors of the direct-fusion method can be found in the papers just cited.

The work presented in this paper was undertaken to gain a more detailed insight into the uranium geochemistry of volcanoes. The hypothetical volatilization of uranium halides from volcanoes (Mason, 1954) was one geochemical mechanism of interest. The possible leaching of uranium from volcanic tuffs was another mobilization mechanism of interest. This study differs from previous work on the volcanic geochemistry of uranium in several respects: (1) the uranium concentrations were determined fluorimetrically; (2) a more detailed study of a single differentiation series was made; (3) strong experimental evidence for secular radioactive equilibrium was found; (4) an attempt was made to follow uranium through a solfataric alteration of the lavas.

Lassen Volcanic National Park, California, was selected for this detailed study because of the large amount of petrographic and chemical data available (Williams, 1932; Day and Allen, 1925; and Nockolds and Allen, 1953; in particular). The accessibility of the area, the presence of fluorite, and the opportunity to compare the fluorimetric uranium analyses with earlier radon analyses (Evans and Williams, 1935) were additional reasons for selecting Lassen.

Sampling

After conferring with Professor H. Williams, the author and Dr. D. F. Saunders collected the samples listed in Tables 2 and 3. The rock nomenclature of Williams (1932) is followed. The sample localities are shown on the accompanying index map, Fig. 1. Hand specimens of the freshest available outcrops were taken in each case with the exceptions of samples 2 and 38, Table 3. Sample 2 was an aggregate of small samples picked up around the mudpots at the Sulfur Works (Sapan's

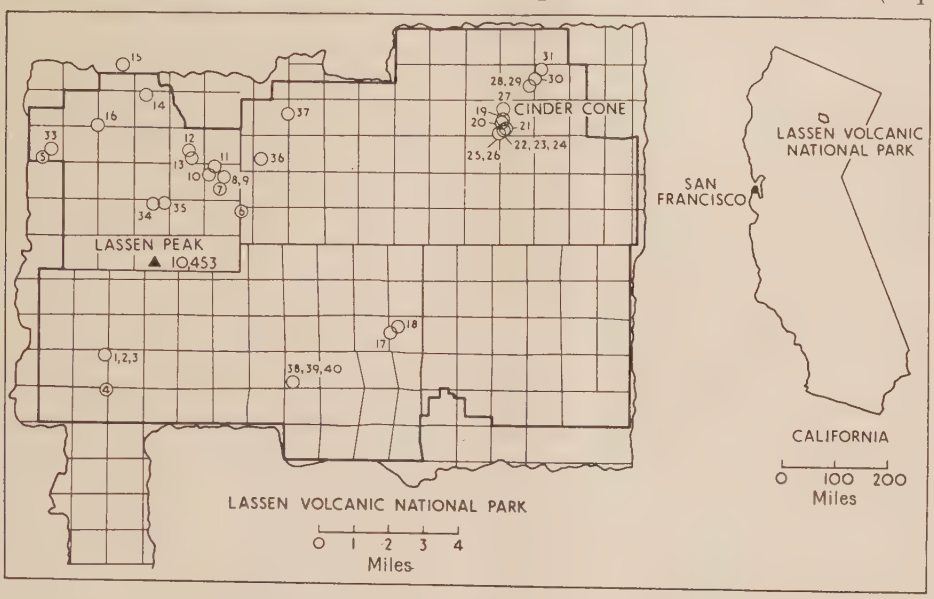

Fig. 1. Index map of California and Lassen Volcanic National Park.

Springs, which is excellently photographed by Day and Allen, 1925). Sample 38 was collected by submerging a gallon polyethylene bottle in one of the mudpots at the Devil's Kitchen. For some of their stay in June, 1952, the collectors were accompanied in the field by Park Ranger P. E. Schultz; the author would like to acknowledge here a debt to him and to the director and staff of Lassen Volcanic National Park for their kind assistance.

Fifty to one hundred grams of each fresh sample were crushed in a steel mortar and ground in a mullite mortar to pass completely through 100-mesh silk bolting cloth. Duplicate samples were ground in several cases, and these demonstrated that the sampling and grinding techniques gave reproducible results. Cases of microuranium contamination have been observed in this and other laboratories, and great care was taken to avoid contamination. The sequence in which the samples were ground and analyzed was always noted, so that possible contamination from unexpectedly high uranium concentrations could be checked.

Method of Uranium Determination

About 1·0 gram of the well-mixed sample was used for each uranium determination. The fluorimetric uranium procedure followed was basically that described by Grimaldi *et al.* (1954). The exact procedure and the results of inter-laboratory

cross-checks are given elsewhere (Adams and Maeck, 1954). The estimated error of the uranium determinations given below is less than ± 15 per cent of the amount present. It should be noted that repeated cross-checks with an isotope dilution uranium determination on the Uncompahgre Granite by Dr. George Tilton agree to within 10 per cent of the 3·4 parts per million uranium found.

Method of Potassium and Sodium Determination

The potassium and sodium determinations given in Table 2 were obtained with a Perkin-Elmer Flame Photometer, Model 52C, using lithium as internal standard. Hydrofluoric and nitric acid treatments were used to open the sample. With this procedure, analysis of National Bureau of Standards Standard Samples Numbers 70, 80, 91, and 99 gave values within ± 4 per cent of the assigned values where more than 0·5 per cent of K_2O or Na_2O was present. The Standard Samples were glasses, clays, and feldspars. The average of duplicate potash and soda determinations is given in Table 2. One of the uranium determinations on each sample in Table 2 was made on an aliquot from the solution used for the alkali determinations.

Method of Measuring Relative Alpha Activities

At least one month after grinding, the relative alpha-particle activity of each powdered (-100 mesh) sample was measured with an alpha scintillation counter (see Curran, 1953, for general principles of this instrument, and Kulp, Holland, and Volchok, 1952, for the applications to minerals). The instrument used was a Scintillscaler, Model CX14, manufactured by Reed and Curtis, Pasadena, California. The prototype of this instrument is described by Reed (1950). The procedure followed was that devised by Ockerman (1954). Counting was continued until a statistical error of less than ± 20 per cent at the 90 per cent confidence level was obtained. The counts were made with the sample in a 2·00-in. diameter dish, giving a sample area of 3·14 sq in. or 20·2 cm^2. The powdered sample was several millimetres thick,

Table 1. *Replicate net alpha counts on sample* 10, *Raker Peak dacite*

Date	*Net alpha counts per hour*	*Total time of counting*
		hours
December 8, 1953	31	17·0
December 18, 1953	35	2·5
December 21, 1953	31	2·0
December 23, 1953	31	2·0
December 28, 1953	27	4·0
December 29, 1953	31	8·0
January 2, 1954	33	4·0
January 5, 1954	33	20·0
January 9, 1954	30	3·3
January 14, 1954	28	4·0
January 28, 1954	26	17·0
February 1, 1954	29	4·0
February 23, 1954	27	18·5
March 8, 1954	29	5·0

giving essentially an infinitely thick alpha source. There was a 2-mm air gap between the surface of the sample and the 2·25-in. diameter ZnS screen. Background counts were taken with the sample dish full of mineral oil, since this substance was found to have a very low intrinsic alpha-particle activity. The background count was measured at least every ten counts, though long experience demonstrated that the background changes very little during the counting of such low alpha activities. In counting the samples listed in Tables, 1, 2, and 3, the background was found to be between one and two alpha counts per hour in every case.

Table 2. *Analyses of rocks from Lassen Volcanic National Park, California*

Sample number	*Rock description*	$\%Na_2O$*	$\%K_2O$*	*Net relative alpha counts/hour**	*Average U in p.p.m.**	*Number of U determinations*
36	Raker Peak pyroxene andesite	3·26	1·26	11	1·0	2
35	Andesite	3·83	1·76	16	1·3	3
37	Twin Lakes andesite	4·13	1·44	16	1·4	3
7	1915 lava with pumice	4·36	1·89	23	1·6	4
17	Flatiron andesite	3·88	1·93	20	1·7	3
18	Pilot Mountain andesite	3·70	1·95	18	1·8	3
15	Table Mountain basalt	3·81	2·05	23	1·9	3
8	Raker Peak dacite	3·80	2·15	26	2·0	4
12	1915 dacite	4·29	2·39	28	2·1	4
13	1915 mud flow	4·27	2·52	34	2·1	4
10	Raker Peak dacite	4·29	2·16	31	2·2	4
16	Chaos Jumbles dacite	4·32	2·53	32	2·2	3
34	Dacite tuff	4·53	2·80	39	2·5	4
11	Raker Peak dacite	4·80	2·65	40	2·6	2
14	Chaos Crags dacite	4·54	2·99	42	3·0	4
5	Manzanita dacite	4·73	2·91	49	3·1	2
33	Dacite pumice	4·43	3·11	46	3·2	3
6	Pre-Lassen dacite	4·58	2·95	47	3·2	3
9	Raker Peak dacite	4·30	3·34	51	3·6	4

* See text for estimation of analytical errors.

In order to check the stability of the Scintillscaler and the precision of replicate loadings of the sample dish, a sample of intermediate alpha activity was selected as an arbitrary standard (Sample 10, Raker Peak Dacite, Table 2). This sample was recounted at short intervals during, and after, the measurements on the Lassen suite (see Table 1). The arithmetic mean of the fourteen determinations in Table 1 is slightly under thirty net alpha counts per hour.

The extreme values are 35 and 26, corresponding to extreme deviations of about 17 per cent from the mean. The standard deviation was 2·5 alpha counts per hour. In the three-month period covered in Table 1, there seems to be a small systematic decline in the net alpha count of Sample 10. This decline could be due to a slight decrease in instrument sensitivity, or to a real decrease in the activity of the sample because of slower radon leakage or some other phenomena. This apparent decline was small compared to the statistical error and the experimental standard

deviation. A value of thirty-one net alpha counts per hour is given for sample 10 in Table 2, because the other Lassen samples were all counted in the first six weeks, covered in Table 1. These data show that the net alpha counts per hour given here are at least as reproducible as the fluorimetric uranium determinations (±15 per cent).

Relative net alpha counts are used in this study because they are quite sufficient to detect significant differences between samples. Furthermore, there were no inter-laboratory standards of comparable rock type and low alpha flux available. The detailed and, at times, sad history of radon measurements (Evans and Goodman, 1941; and Davis and Hess, 1949) and of chemical analysis of rocks in general (Fairbairn *et al.*, 1953) demonstrate that absolute inter-laboratory comparisons can only be made on thoroughly homogenized and carefully analyzed standards. To facilitate later comparisons, National Bureau of Standards Sample 787, the monominerallic Carthage limestone was counted with the Lassen samples. A relative net count of 3·5 alphas per hour was obtained.

Table 3. Additional uranium analyses and relative alpha activities

Sample number	*Sample description*	*Relative alpha counts per hour**	*Uranium in parts per million*	*Number of replicate uranium determinations*
34	Dacite tuff, Crescent Crater	41	3·1	2
40	Clay from Mudpot, Devil's Kitchen	36	3·0	4
25	Andesite, Painted Dunes	25	3·0	2
28	Quartz basalt, Old post-Cinder flow	22	2·5	3
38	Clay and water from Mudpot, Devil's Kitchen	23	2·3	4
2	Aggregate sample from Devil's Kitchen	33	2·2	4
27	Volcanic ash, Cinder Cone	26	2·1	3
30	1915 Lava with pumice	22	2·1	4
26	Volcanic ash, Painted Dunes	24	2·0	3
39	Quartz basalt bomb, Cinder Cone	16	2·0	2
4	Brokeoff Andesite Unaltered	24	2·0	4
29	Diatomaceous Earth, near Butte Lake	11	1·8	3
23	Andesite, 1851 flow, altered (?), Cinder Cone	21	1·7	2
24	Vesicular basalt, Cinder Cone	19	1·7	2
39	Flatiron andesite (altered) Devil's Kitchen	18	1·7	3
19	Ash, Cinder Cone	18	1·7	4
22	Quartz basalt, source of 1851 flow, Cinder Cone	18	1·6	2
20	Ash, Cinder Cone	28	1·4	3
31	Eastern basalt, Butte Lake	8	0·86	3
32	Pahoehoe Lava, Subway Cave (outside Lassen Park)	2	0·36	4

* See text for estimation of analytical errors.

Experiments indicate an effective geometry of about 32 per cent for the instrument used (Reed, 1950; and this laboratory). The relative net counts per hour given in Tables 2 and 3 can be converted to estimated total alpha particles/square centimetre/hour by dividing by 12. The figure obtained would represent the number of counted alpha particles coming off the surface of the sample, not the total alpha flux in a given volume of the sample. The total alpha flux would depend upon a number of factors (see Nogami and Hurley, 1948), including the distribution of the alpha emitters and the absorption of the sample. Nogami and Hurley also discuss the merits of thick- versus thin-source alpha counting. The Lassen samples are well suited to thick-source alpha counting, because they are fine grained and, as is shown below, their alpha-particle activity is largely concentrated in the glassy phase.

Discussion

Relationship of Radium and Uranium

The radon concentrations of the Lassen suite were determined by Evans and Williams (1935). From their radon measurements they calculated the radium concentrations in twelve Lassen rocks. These values ranged from $0{\cdot}28 \times 10^{-12}$ gram/gram in basic lavas to $1{\cdot}14 \times 10^{-12}$ gram/gram in the more silicic lavas, with an observational uncertainty of $0{\cdot}02 \times 10^{-12}$ gram/gram. The equilibrium amounts of uranium would then range from 0·79 to 3·20 parts per million (10^{-6} gram/gram). The fluorimetric uranium analyses, which were made on an entirely independent sampling of the Lassen suite, range from 0·85 to 3·6 parts per million (see Tables 2 and 3), with an estimated uncertainty of less than ± 15 per cent of the amount present. A comparison of the equilibrium uranium values calculated from the radium values of Evans and Williams (1932) and the fluorimetric uranium values is given in Table 4. Four of Evans and Williams's samples are not listed, because comparable samples were not collected and analyzed fluorimetrically.

Table 4 indicates excellent overall agreement between the two methods of uranium determination. The largest difference, 0·79 versus 2·0 p.p.m., is in the Brokeoff andesite, Sample 4. This large difference may represent a real difference in the sample similar to the difference Evans and Williams found in the Chaos Crags dacite and to the difference found in the Raker Peak dacite (see Table 4). However, the Brokeoff andesite values differ by 250 per cent of the lower value, whereas the difference in the Raker Peak dacite values is only 80 per cent of the lowest value. Any contamination after sampling would have to be of a very special type, since Sample 4 has the same relative alpha-particle activity to uranium ratio as the other Lassen samples (see below). This ratio, and the fact that the Brokeoff andesite is one of the older flows, suggest that radon and uranium are probably in equilibrium, and the difference is not due to a loss of radon. Examination of Table 4 will show that 2·0 p.p.m. uranium cannot be considered an unusually high value for a Lassen andesite. A petrographic examination of a thin section of Sample 4 showed no radical difference from the description given by Evans and Williams. It is believed that Sample 4 may be from one of the more

dacitic parts of the Brokeoff andesite as described by Williams (1932) and that Evans and Williams determined radon on a less dacitic part.

Aside from the Brokeoff andesite, the other seven examples show good agreement between the fluorimetric and calculated uranium determinations, although the two analyses were made on different samplings. The comparisons in Table 4

Table 4. Comparison of direct-fusion and fluorimetric uranium determinations

Fluorimetric			*Direct-fusion* (Evans and Williams)		
Sample No.	*Rock description*	*U in p.p.m.*	*Sample No.*	*Rock description*	*U in p.p.m.*
31	Eastern basalt, Butte Lake	0·86	2	Basalt, NE Butte Lake	0·98
36	Raker Peak andesite	1·0	5	Andesite, Raker Peak	1·01
17	Flatiron andesite, Pilot Mountain	1·7	9	Andesite, Crystal Lake	1·96
4	Brokeoff andesite	2·0	6	Andesite, Brokeoff Volcano	0·79
12	1915 dacite	2·1			
13	1915 mud flow	2·1	11	Dacite (1915) Lassen Peak	1·96
7	1915 dacite + pumice	1·6			
30	1915 dacite + pumice	2·1			
16	Chaos Crags dacite	2·2	13	Dacite, Chaos Crags	1·97 2·64
33	Dacite pumice, Lassen Peak	3·2	8	Dacite pumice, Lassen Peak	2·24
8	Raker Peak dacite	2·0	14	Dacite, Raker Peak	3·20
10	Raker peak dacite	2·2			
11	Raker Peak dacite	2·6			
9	Raker Peak dacite	3·6			

are made on samples taken from a few yards to nearly four miles apart. Except for the Brokeoff andesite, all differences between the two sets of values can be easily accounted for on the basis of analytical errors and variations within the rock. Each set of data has an example of variation within a rock unit, and the Raker Peak case is particularly convincing because the variation in uranium content is paralleled by a variation in potassium content as is discussed below.

The data in Table 4 indicate that the relationship between uranium and radium in the Lassen suite is one of secular equilibrium to within analytical error. These data also independently confirm the direct-fusion method of uranium determination in samples of this type.

Relationship of Uranium and Potassium

Evans and Williams (1935) found a positive correlation between radium and potassium in the Lassen suite. In the Chaos Crags dacite they found most of the radium concentrated in the potassium-rich glass phase first described and analyzed by Hague and Iddings in 1883. A very definite positive correlation between

potassium and uranium is found in the samples listed in Table 2 (see Fig. 2). Allowing for a ± 10 per cent error in the uranium determination, a straight line can be made to pass through all nineteen points in Fig. 2. This linearity is preserved in the four samples of the Raker Peak dacite (Samples 8, 9, 10, and 11). The glassy phase then is the main carrier of potassium, radium, uranium, and

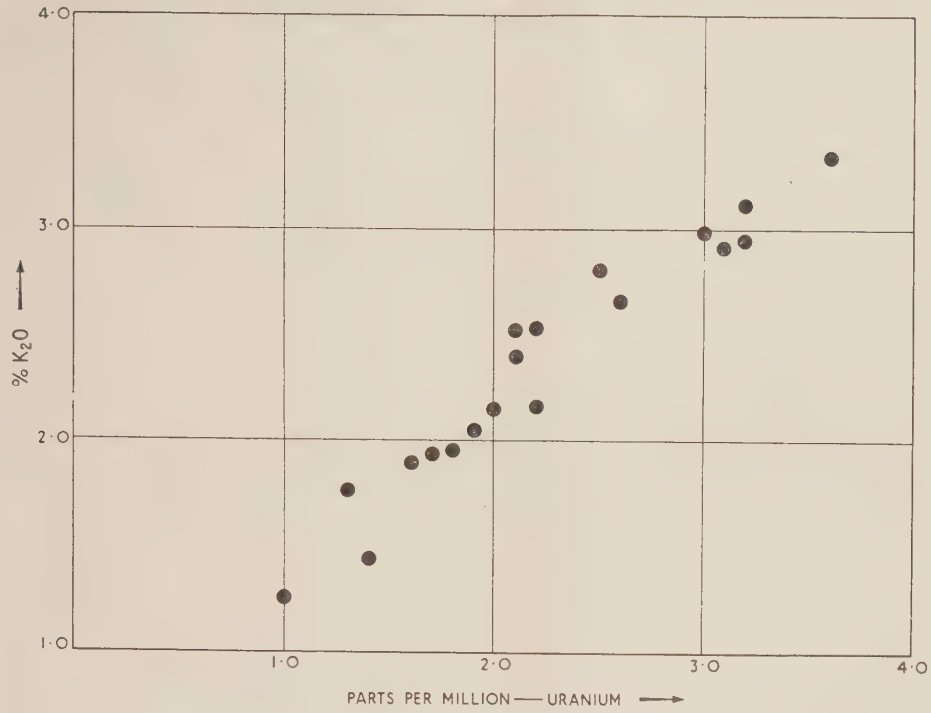

Fig. 2. Uranium versus potash.

probably thorium. These data do not exclude the possibility that the uranium is contained in very small crystals, e.g., zircons, within the glass (see below). This very linear relationship between potassium and uranium can be interpreted in terms of fractional crystallization with the exclusion of these elements from the crystalline phases formed and separated from the magma. The ionic size and co-ordination number with respect to oxygen of potassium and uranium are consistent with such an interpretation. The slope of a trend line in Fig. 2 is about 0·75 (K_2O in percent, U in p.p.m.), indicating that uranium was excluded more effectively than potassium from the crystalline phases precipitated from the magma. The correlation between potassium and uranium is another general form of expressing the correlation between silica and uranium, since both silica and potassium increase in the residual magma during the first stages of magmatic differentiation. It seems unlikely that there was any loss of uranium to a gaseous phase at Lassen, for a loss of uranium would deplete uranium relative to potassium in the later differentiates. The actual case is that uranium was concentrated relative to potassium in the later stages by the removal of some potassium into the

crystalline phases. These last observations agree with the conclusions of Mason (1954) regarding the unlikelihood of uranium halides forming under volcanic conditions where the rocks are molten.

If the "original magma" had a uranium content similar to the least uraniferous Lassen basalt (about 0·8 p.p.m.), and if fractional crystallization was the

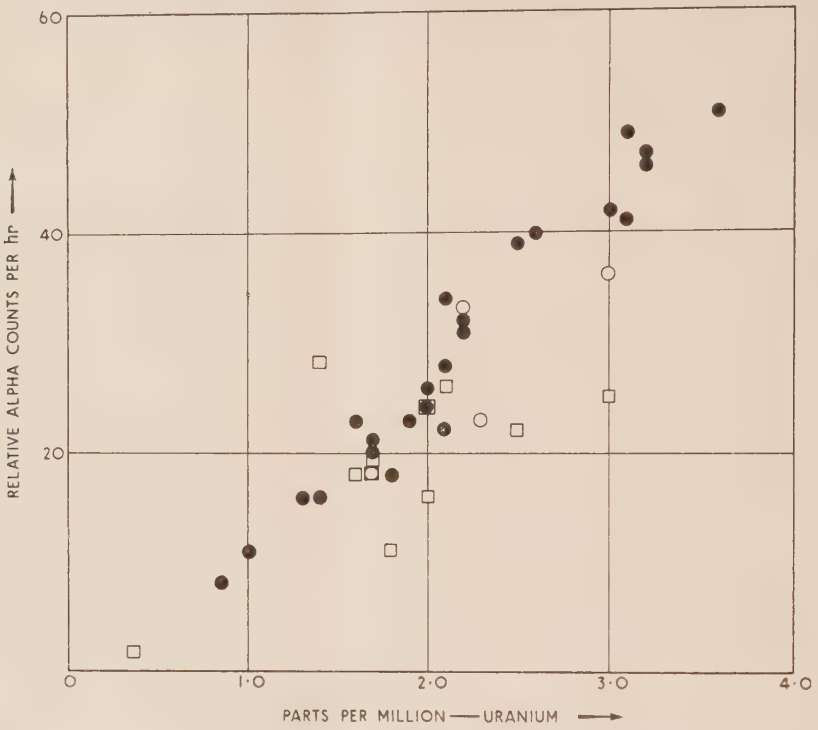

Fig. 3. Uranium versus relative net alpha activities.

dominant mechanism, the Raker Peak dacite represents about 25 per cent of the volume of magma from which its uranium was derived. This figure of 25 per cent is similar to the figures obtained in analogous calculations made by Wager and Mitchell (1953) on the basis of trace element analysis of Hawaiian lavas. If the pahoehoe lava from Subway Cave, a few miles outside Lassen Park, is representative of the uranium content of the "original magma," the Raker Peak dacite represents only about 10 per cent of the volume of magma from which its uranium was derived.

Relation of Thorium, Uranium, and Relative Alpha Activity

A plot of the net relative alpha-particle activity versus uranium content of each sample is shown in Fig. 3. The solid circles represent the unaltered Lassen volcanics, and the open circles represent altered Lassen volcanics, including mud-pot clays. The open squares represent the Cinder Cone lavas and tuffs and the pahoehoe lava from Subway Cave. Pairs of values from these three groups fell

on the same point in a few cases. The main Lassen sequence (solid circles) shows a strong positive correlation between uranium content and relative alpha activity. The relative alpha activity is a measure of a complex of phenomena involving over twenty different alpha-emitting nuclides in the U^{238}, U^{235}, and Th^{232} decay series. Many of these nuclides contribute so little to the total alpha-particle activity that they may be omitted from this discussion. Thus, the entire U^{235} series may be neglected because it contributes only about 4 per cent of the total alpha activity from both uranium series, and about 2 per cent of the total activity from the U^{238}, U^{235}, and Th^{232} series at radioactive equilibrium, assuming a Th/U ratio of 3.

The interpretation of the relative alpha-particle counts is further simplified if radioactive equilibrium exists. Radioactive equilibrium probably exists in the Lassen samples, because U^{238} and Rn^{222} are in close equilibrium where they have been measured (see above and Table 4). This equilibrium could only exist if all intermediate members of the series are in equilibrium. If the U^{238} series is in equilibrium through Rn^{222}, the rest of the series requires only a hundred years or so to come to equilibrium. The entire Th^{232} series requires less than a hundred years to come to equilibrium.

Assuming for these samples that radioactive equilibrium exists in the U^{238} and Th^{232} series, it follows from the decay scheme that for each alpha particle emitted from U^{238}, seven alpha particles are emitted from the other members of the series on the average. Similarly, for each alpha particle emitted from Th^{232}, five alpha particles will be emitted from the other members of that series on the average. Since the specific activity of Th^{232} is about one-third that of U^{238}, we may write as a first approximation:

$$\begin{matrix}\text{number of alpha} \\ \text{particles emitted}\end{matrix} = 8_U + \frac{K6_{Th}}{3} \qquad (1)$$

where $K = \text{Th/U}$. K is equal to about 3 in most types of rocks and meteorites. From equation (1) it follows that at equilibrium change of the Th/U ratio from 3 to 2 would reduce the number of alpha particles emitted by about 14 per cent. Thus, the total alpha particles emitted to uranium ratio is a rather insensitive measure of Th/U ratios.

Another point to be considered is the relation between the total number of alpha particles emitted, and the relative alpha count measured. The alpha particles from the U^{238} and Th^{232} series do not have the same energies, and thus their likelihood of being counted is not the same (see Nogami and Hurley, 1948). No correction for this difference in energies is made here, because the precision of the data does not justify it. If a Th/U ratio of 3 is assumed in the average Lassen sample, it is unlikely that the Th/U ratio has been shifted to less than 2 or to more than 4 during differentiation. Kirsh and Hecht (1938) believed that differentiation finally separates thorium and uranium, but the data presented here give no indication that this separation has begun to take place at Lassen.

The Cinder Cone samples in Fig. 3 (open squares) show the widest deviations from the main trend. This may have been caused by selective leaching of uranium from some of the weathered samples. Their deviating from the main Lassen sequence is not inconsistent with the view of Finch and Anderson (1930) that

these are contaminated rocks. Some of the open circles in Fig. 3 are well off the main trend, and these are weathered Lassen lavas; selective leaching of uranium is probably the cause. The open circles in Fig. 3, that are on the main Lassen sequence, are samples of mud-pot clay. This would indicate that the mud-pot clays had about the same Th/U ratio and degree of radioactive equilibrium as the main Lassen sequence, which is surprising considering the extreme weathering taking place in the hot, acid mud-pots. It was hypothesized that zircons in the mud-pot clays were responsible for much of the observed uranium concentration and alpha particle activity. The autoradiographic work of Picciotto (1950) on European igneous rocks showed that much of the uranium in these rocks was contained in zircons, as well as sphene and apatite. Evans and Williams (1935) reported zircons in some of the Lassen mud pots, and Hague and Iddings found zircons and apatites in the Lassen dacite.

Zircons were separated by means of carbon tetrabromide from mud-pot clay Samples 38 and 40 in Table 3. The zircons separated were single crystals 10 to 30 microns parallel to the *c*-axis and 5 to 10 microns perpendicular to the *c*-axis. It was not difficult to locate zircon specimens in the heavy mineral separate. Most examples had the common prismatic and pyramidal forms, though some appeared corroded. Most of the zircons observed were quite transparent, but one liquid inclusion and some mineral inclusions, perhaps thorite, were noted. Quantitative attempts were made to separate the high-density minerals from the mud-pot clay. The alpha activity of the low density fraction and the uranium content of the tiny, heavy mineral separate could then be determined. Both sodium-hydroxide size segregation (Pennington and Jackson, 1947) and carbon-tetrabromide methods were tried with inconclusive results. With the best separation achieved, the relative alpha activity of the light-clay fraction was decreased about 50 per cent.

The zircons, together with similar resistant minerals and rock fragments, are believed to contain the uranium found in the mud-pot clays. These materials would also be capable of retaining the uranium daughters and the thorium series, so that the material would have a uranium to alpha-activity ratio characteristic of the Lassen suite (Fig. 3).

Conclusions

The main conclusions of this study are:

(1) The direct fusion and fluorimetric methods of uranium determination agree closely on the uranium content of the Lassen suite of rocks.

(2) This agreement is both a result and a proof of secular radioactive equilibrium between radon and uranium. This equilibrium implies that there is radioactive equilibrium throughout the thorium and uranium series in these rocks.

(3) During differentiation at Lassen, uranium, potassium, and probably thorium were concentrated in the residual magmas at almost the same rate. Fractional crystallization is adequate to explain the observations.

(4) Some of the uranium of the Lassen lavas is present in small zircon crystals.

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Chemical energy and metamorphism

Vincent A. Saull*

ABSTRACT

Data on heats of reaction indicate that metamorphic chemical changes may in certain cases develop temperature rises of several hundred degrees centigrade. From this evidence, and from geological reasoning, it appears that metamorphism may be fundamentally a spontaneous exothermic chemical process, the initiation and general character of which depend upon kinetic factors.

A consistent terrestrial energy economy can be built around this theme, on the basis that the chemical energy of metamorphism is solar energy which has been stored during rock weathering.

Contents

PAGE

Introduction 86
The sign of the heat effect in metamorphism 86

I. Enthalpy Changes in Metamorphic Processes 87
A. Experimental data 87
B. Indirect evidence of the sign of the heat effect in metamorphism . . . 96

II. Kinetics 99
A. Kinetics of chemical change 99
B. Kinetics of heat flow 100
C. Experimental data 101
D. Discussion 102

Acknowledgements 104

References 105

Introduction

In the present paper it will be shown that a theoretical investigation of enthalpy changes in metamorphism leads to interesting conclusions concerning the geologic role of energy stored chemically, by geologic processes.

The sign of the heat effect in metamorphism

Evidence is presented below that many fundamental anamorphic changes are exothermic. Most geologists seem to consider it as axiomatic that anamorphism is an *endothermic* process. Nevertheless, there is no experimental or theoretical basis for this assumption, which gives rise to many vexing problems, and solves none. Rather, this assumption seems to originate in a failure to distinguish between the roles of heat which may be required to make a physico-chemical change thermodynamically possible, and heat which accelerates sluggish but *already spontaneous* changes.

* Geology Dept., Massachusetts Institute of Technology. At present, Assistant Professor, Dept. of Geological Sciences, McGill University, Montreal, Canada.

To clarify this point, attention is called to the sharp difference between thermodynamic stability and what may be termed inertness or kinetic stability.

A thermodynamically stable state is one which remains unchanged, *no matter how long we watch it*, or to what small perturbations we subject it. The stable state has a lower Gibbs free energy than any other state of the system under the same conditions of temperature and pressure.

An inert state is a metastable one, which owes its apparent stability solely to the sluggishness of the changes which might alter it to a more stable state. It may remain unchanged for a long time, even when subjected to perturbations, but eventually it will revert to some other state. The Gibbs free energy of such a state is not the lowest possible for the given system under the given conditions.

Inert systems are extremely common, and are of the greatest practical importance. For example, steel, glass, coal, and oil are all thermodynamically unstable in the environments in which they are ordinarily kept, and the kinetic factor alone makes it possible to use these materials as we do. Inert systems seem to have a corresponding importance in geology. For example, studies of authigenic mineral formation indicate that the "equilibrium" concept is incomplete, in that numerous "high temperature" minerals form authigenically (SERDYCHENKO, 1949; SOBOLEV, 1951).

When the kinetic factor is considered, it is seen that much of the supposed geologic field evidence for endothermic anamorphism is inconclusive. It is true that, where there is evidence that thermal or mechanical energy has been available, there is metamorphism. However, this does not prove that metamorphism is endothermic any more than the scorching of paper by a hot iron proves that scorching is endothermic; or than the fact that it is necessary to "strike" a match to light it proves that the resulting ignition is endothermic. The facts are equally well explained if it is assumed that the initial rock material is inert in the above sense, and that the metamorphism is due to local catalysis. Again, there are many instances of metamorphism where there is no evidence that thermal or mechanical energy has been available, and this has been the subject of much involved discussion in the literature.

Certain types of anamorphism, or certain stages of the anamorphic process, can be and are endothermic. Only experimental work can give the complete picture. Here, as a prelude to the presentation of data, the point which requires emphasis is that there is no basis for the generalization that anamorphism is always endothermic.

I. Enthalpy Changes in Metamorphic Processes

A. *Experimental Data*

Data are presented below for the enthalpy changes in certain examples of the following metamorphic processes:

1. Devitrification.
2. Recrystallization.
3. Chemical reaction:
   (a) Salt reactions,
   (b) Sulphide and oxide reactions,
   (c) Silicate reactions.

In the usual way, the enthalpy change is a measure of the heat produced or absorbed at constant pressure.

All the physico-chemical heat effects of metamorphism are of course not included in the above grouping. Depending upon the phases present, upon the extent to which local systems are open, on the pressure and volume, etc., there must be considered also such effects as solution, sublimation, dilution, diffusion, and mechanical work. However, the processes considered include the most important metamorphic processes, and provide a basis for preliminary discussion of chemical energy in metamorphism. All the above changes occur, or conceivably could occur geologically, in closed systems, and at a low pressure, and therefore the enthalpy changes given are of fairly direct geologic significance.

The data given have been obtained entirely through literature search. Transformations of geologic significance have not been much studied by thermochemists, and, owing to measurement difficulties, the values obtained are in most cases not precise.

1. *Devitrification*

The glassy state is a rarity in physics as a whole, being possible only in one element, selenium, and in a few oxides and oxy-salts. The importance which this state has in geology is of course due to the glass-forming properties of the silicates.

Present ideas of the glassy state, and the reason for it, are very similar to those first expressed by ZACHARIASEN (1932).

Briefly, all glasses have as primary structural elements certain closely-knit groups, such as SiO_4, BO_3, and PO_4. These join by sharing corners, edges, and faces, but the exact manner in which they do so is of minor importance.

Glasses may therefore be thought of as possessing short-range order—within the structural unit, or through a few units—but exhibiting randomness on a broader scale. In this condition, a glass-former has less excess energy relative to its crystalline counterpart than a non-glass-former would have. Nevertheless, the glassy state is a high energy state, and the formation of glass seems in every case to be due to rapid cooling to below the temperatures at which the devitrification rate is measurable.

In Table 1, data on devitrification heats are tabulated. Where the original reference has given heats of fusion, these have been converted to devitrification at 20°C, using interval heat capacities given by BIRCH (1942).

The calculation of the heat rise due to devitrification at 20°C has been made assuming that the specific heat has a constant mean value. In most cases the specific heat value used has been taken from BIRCH (1942). The data given are to be regarded as approximate only. A good idea of the variability possible in measurements may be gained from the notes accompanying the relevant data given by BIRCH.

Particularly striking in Table 1 is the discrepancy between the value for devitrification of quartz obtained by RAY (1922) and those obtained by MULERT (1912) and WIETZEL (1921). Because this point bears on the method of differential heat of solution in general, and also on the surface and strain energy factors which are to be discussed below, it will be considered in greater detail.

The above discrepancy is believed to be due primarily to greater specific surface and strain energy in the material used by MULERT and WIETZEL in their measurements than in the material used by RAY. RAY used silica of about 20–40 mesh. By employing an excess of solute, and quenching the solution process with water, he was able to achieve relatively high solution in short time. MULERT and WEITZEL, on the contrary, used the method of total solution, and owing to the slight solubility of silica, they has to use very finely ground material to obtain measurable

Table 1. *Enthalpy change accompanying devitrification of mineral glasses at* 20°C

Material	*Composition*	*T* °C	$-\Delta H$ kcal/mole	$-\Delta H$ joules/gram	$-\Delta H_{20}$ joules/gram	ΔT_{20} °C	*Reference*
Quartz	SiO_2	20	2·21	154·1	154·1	185	Wietzel (1921)
		20	2·32	162·3	162·3	190	Mulert (1912)
		20	6·95	485·4	485·4	480	Ray (1922)
		20	3·33	233·0	233·0	268	Bichowsky (1936)
Adularia	$KAlSi_3O_8$	20	—	348·0	348·0	390	Mulert (1912)
Microcline	$NaAlSi_3O_8$	20	—	418·0	418·0	440	Mulert (1912)
Leucite	$KAlSiO_4$	20	—	109·0	109·0	140	Mulert (1912)
Rhodonite	$MnSiO_3$	20	8·52	271·0	271·0	260	Mulert (1912)
Willemite	Zn_2SiO_4	20	9·04	170·0	170·0	190	Mulert (1912)
Enstatite	$MgSiO_3$	1524	—	616·0	633·0	630	Birch (1942)
Wollastonite	$CaSiO_3$	1512	—	528·0	258·0	260	Birch (1942)
Diopside	$CaMgSiO_3$	1391	—	340·0	383·0	380	Birch (1942)
Anorthite	$CaAlSi_2O_8$	1550	—	440·0	675·0	650	Birch (1942)
Albite	$NaAlSi_3O_8$	1105	—	203·0	140·0	150	Birch (1942)

Key: T—The temperature at which the transmission was measured.
ΔH—The enthalpy change accompanying the transition at T°C.
ΔH_{20}—The enthalpy change accompanying the transition at 20°C.
ΔT_{20}—The adiabatic temperature increase attending devitrification of the material at 20°C.

solution. (Mulert ground his material for seventeen hours, and then separated the fines in water, ending up with one gram of usable material per kilogram of original material. Wietzel ground his material for one hundred hours in a mechanical mortar.)

The assumption that the difference in his results from those of the earlier investigators is due to the difference in grinding was checked experimentally by Ray, with the following results.

Table 2. *The effect of grinding on the heat of solution of quartz*

Material ↓ *State* →	*Heat of solution in kilocalories/mole*		
	20–40 *mesh*	15 *hrs grinding*	*Difference*
Quartz glass	37·24	36·95	0·29
Quartz crystal	30·29	32·46	2·17

(The above heats of solution are in 35 per cent HF).

Ray suggested that grinding had vitrified part of the crystalline material, thereby increasing its specific energy. He was unable to explain the decrease in energy shown by the glass after grinding, because X-ray work by separate investigators failed to show crystalline material which might have decreased the energy.

The writer feels that there need be no real anomaly in the above results. The factors concerned are surface energy and strain energy. Grinding of quartz crystal is certain to increase its energy, because it must increase the surface area, and also disrupt the low-energy crystalline state. The effect of grinding on the glass is not

so easily predicted. First, grinding might have an annealing action on glass, and produce a rude crystallization too imperfect to be detected by X-ray methods. Second, the specific energy of the atomic complexes near the particle surfaces may actually be less than the specific energy of complexes within the glass particles. There is some evidence that rather low-energy configurations—at least relative to the glassy structure—are realized on fracture surfaces (BUERGER, 1951). At any rate, grinding is not to be expected to have the same effect upon glassy as upon crystalline material.

Experimental error is a third possibility, but is unlikely to be the dominant factor, because the effect was reproducible. RAY'S experimental arrangements were certainly cruder than those of MULERT and WIETZEL, but on the other hand the temperature changes actually measured by WIETZEL and MULERT in their calorimeters were of the order of one degree centigrade, while RAY states that none of the temperature changes that he observed was lower than 6°C, and that some were as high as 34°C. Finally, recent preliminary measurements, made under the writer's direction at McGill University, using modern equipment, give values of the same order of magnitude as those of Table 2.

2. *Recrystallization*

Recrystallization is defined here as a process by which a crystal aggregate decreases its specific surface area, or by which internal strains are dissipated. Thus, a net decrease in surface energy or strain energy is involved. Such phenomena are, of course, widespread in metamorphism, but are most obvious in monomineralic materials, such as gypsum, limestone, halite, and sandstone.

The underlying principles of this type of recrystallization have been discussed by BUERGER and WASHKEN (1947) as a preface to experimental work on recrystallization of several monomineralic powders. A more lengthy treatment is that of GEISLER (1951), which relates chiefly to metals.

That there is a tendency for crystalline aggregates to minimize their specific surface and strain energy is theoretically certain. More important for practical purposes is the experimental fact that such energy actually appears to be capable, under suitable conditions, of driving the recrystallization. This is shown by the above work of BUERGER and WASHKEN, and, on a more general scale, by similar sintering experiments in ceramics and metallurgy.

The origin of the compaction tendency is considered to be primarily the excess surface energy of the powder, relative to that of the compacted forms (see, for example, MACKENZIE and SHUTTLEWORTH, 1949). Strain energy is believed by most authors to be less important, at least in metals, because it is less readily stored in the structure. Quantitative measurements on the role of the surface energy in sintering have been made by SHALER and WULF (1948), with the result that surface energy is considered to be sufficient to drive the observed changes.

In Table 3, the approximate heat of recrystallization, and the adiabatic temperature rise which would result from recrystallization, are listed for certain materials. By heat of recrystallization is meant the heat which would be released if the material in question were to become a single, unstrained crystal.

The values in Table 3 are orders of magnitude only. For any particular material, the exact value would depend on the precise initial and final states. The heat of recrystallization values is greater for the harder materials. This is predicted by theory, because hardness is a reflection of bond strength. The initial and final states of the different materials listed do not necessarily correspond exactly, however, and it is therefore unwise to emphasize this hardness-heat relation.

Table 3. Standard enthalpy change and adiabatic temperature rise in certain materials due to release of surface and strain energy

Material	$-\Delta H$(*cal/mole*)	*T rise* (°C)	*Reference*
NaCl (sublimate)	12	1·0	Lipsett (1927)
NaCl (ground)	30	2·5	Lipsett (1928)
ZnO	1,150	120·0	Hedvall (1934)
Fe_2O_3 (hematite)	4,700	185·0	Hedvall (1934)
Quartz	2,170	180·0	Ray (Table 2)
Quartz	4,740*	370·0	Ray (Table 1)*
Chalcedony	3,070	245·0	Wietzel (1921)
Colloidal SiO_2	5,330	390·0	Bichowsky (1936)
Colloidal SiO_2	8,870	580·0	Bichowsky (1936)
Fe_2O_3 ("amorphous")	13,500	425·0	Fricke (1936)

* Calculated on the assumption that the difference between Ray's and Mulert's values for devitrification of quartz glass (Table 1) is entirely due to surface and strain energy.

As a complement to the above surface energy data, the following table of surface areas is of interest.

*Table 4. Surface area of certain materials, in sq m per gram**

No.	*Material*	*Area*	*No.*	*Material*	*Area*
1	Fine red silt	2·0	10	$BaSO_4$ ppt.	4·30
2	Fine inorganic limestone	40·0	11	Montmorillonite and kaolinite	15·5
3	Deep water red clay	25·0			
4	Deep water green clay	10–15	12	"Cecil soil 9418"	32·8
5	Mica (0·1 mm sheets)	0·02	13	Halloysite	43·2
6	$CuSO_4 . 5H_2O$ (40–100 mesh)	0·16	14	Illite	97·1
7	KCl (200 mesh)	0·24	15	Silica gel	584·0
8	Pumice	0·38	16	"Darco G"	2123·0
9	Cement	1·08			

* From Kulp and Carr (1952).

3. *Chemical reaction*

When considering the heat effect of a geologic reaction, it is in many cases difficult to be certain just what reaction has taken place. Detailed geologic study is always able to give information on the products of reaction remaining in the rock, but does not always reveal unequivocally the reactants, or the reaction mechanism, or products which may have disappeared from the system.

The data in the following table merely indicate some reactions which *could* occur, and in most cases the data should be considered as giving only an idea of the magnitude of the heat effect. This is particularly so for salt and sulphide reactions. Such reactions occur for the most part in regions of high ionic mobility, and it is difficult to be certain of the reactants involved, or the reaction mechanism.

(a) *Salts*—The difficulty in attempting to determine the heat effect of reactions between salts, in the diagenetic environment, is, again, to know the actual reaction.

The systems concerned are usually open, which affects both the equilibria obtaining, and the enthalpy changes. Because the heat of reaction for the closed system may be rather small, subsidiary heat effects are important, and it is difficult to make predictions. Of the reactions listed in Table 5, perhaps only number 4 is correctly written.

*Table 5. Standard enthalpy change and adiabatic T rise in some salt reactions**

Reaction	$-\Delta H$ (kcal)	T(°C)
1. $CaCO_3 + MgCO_3 \rightarrow CaMg(CO_3)_2$	2·2	60
2. $CaSO_4 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O$	5·0	110
3. $2CaCO_3 + MgSO_4 \rightarrow CaMg(CO_3)_2 + CaSO_4$	0·21	4
4. $CaCO_3$ (aragonite) $\rightarrow$ $CaCO_3$ (calcite)	−0·04	−2

* Data from BICHOWSKY and ROSSINI (1936).

The reaction aragonite—calcite is endothermic, but its observed occurrence does not necessarily refute the present hypothesis concerning the sign of the heat effect in metamorphism. This is discussed below, in Section B(1).

(b) *Oxides and sulphides*—The same difficulty, that of writing reactions that actually occur in metamorphism, and not merely ones for which heat data are available, presents itself here. Such phase changes as high to low chalcocite are known to occur, but these are relatively rare, and in most cases the associated heats are small. A few values are listed in Table 6.

Table 6. Standard enthalpy change and T rise in some oxide and sulphide reactions

Reaction	$-\Delta H$ (kcal)	ΔT(°C)
1. $Al_2O_3 + 3H_2O \rightarrow 2Al(OH)_3$	9·7	260
2. $2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O$	7·46	95
3. ZnS (wurtzite) $\rightarrow$ ZnS (sphalerite)	3·19	250

References: 1. ROSSINI, F. D., *et al.* (1952).
2. ROSSINI, F. D., *et al.* (1952).
3. KAPUSTINSKY and CHENTZOVA (1941).

(c) *Silicates*—Silicate reactions are by far the most important from the point of view of this paper. This is because most metamorphic reactions are silicate reactions, and also because both theory and experiment indicate that the heats of silicate reactions are much higher than those of corresponding salt and sulphide reactions.

Direct heat data have been located for only one silicate reaction which might be important in metamorphism: the break-up of kaolinite to form sillimanite, quartz, and water.

Most of the reaction heats have been determined by MULERT (1912). The

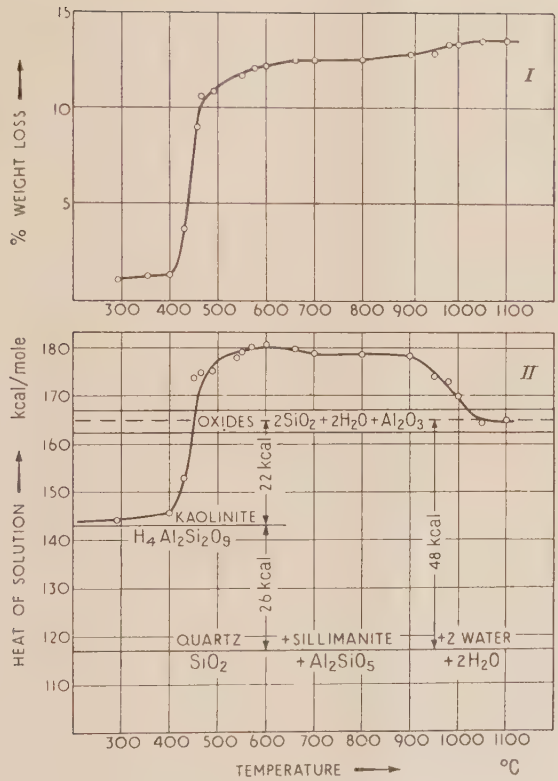


Fig. 1. Heat of solution of dehydrated kaolin (KLEVER, 1930).

values given are probably considerably in error, as is suggested by the large difference between the heats of formation listed for "microcline" and "adularia." Also, it is obvious that the reactants do not represent naturally-occurring minerals. The sole exception to this is the reaction between Al_2O_3 and SiO_2 to form sillimanite. These occur as natural minerals, and corundum is frequently associated with quartz in modern sands. The adiabatic temperature rise for this reaction would be approximately 1000°C. (It is to be noted that, in this case, the reaction energy has not been directly stored by weathering, but is attributable to the source which formed the parent rocks.)

The other reactions of part *A* have little direct geologic significance. The natural reactants for the formation of, say, authigenic feldspar, are certainly not anhydrous oxides, but rather some sort of illitic clay-materials, with indefinite structure and composition. The real transformation possibly cannot be even approximated by non-geologic material, but it is slightly more realistic to consider hydrated oxides as reactants, and this is done in parts *B* and *C*. Because the hydration reactions (*B*) are exothermic, the combined reactions (*C*) have smaller heat effects than the corresponding anhydrous ones.

The actual moderating effect of water on the heat of reaction would not be expected to be so large as indicated in the table, because it is unlikely that the heterogeneous geologic material would achieve such a low energy state as the hydroxides considered. This would certainly be true once the material had been somewhat compacted. The effect of water is more realistically indicated by the data of KLEVER (1930A) which are discussed below.

The fact that equation (19) of Table 7—the formation of wollastonite from silica and calcite—is endothermic, does not refute the hypothesis of exothermic anamorphic reactions. This is characteristically a contact metamorphic reaction, and, in most field occurrences, the source of the required energy is apparent. Contributing to the realization of reaction 19 is, of course, the removal of the gaseous product CO_2.

Because of its direct geologic significance, reaction 20 of Table 7 will be discussed in detail. KLEVER (1930A) determined his heat values from differential heats of solution in 40 per cent HF. The material used was Zettlitz kaolin, stated to be 98·5 per cent pure. The impurities were disregarded in the calculations, and the ideal formula $H_4Al_2Si_2O_9$ used. Dehydration was achieved by heating for six minutes in an air-stream dried with sulphuric acid and phosphorus pentoxide. Final values used in the determinations are the means of sets of two or three determinations. From the data given in the original paper, the maximum deviation from the mean is of the order of one or two per cent. The effect of the water content on the solution heat is small—of the order of 0·5 kilocalories per mole (KLEVER, 1930B)—and may be disregarded.

Study of the thermal changes accompanying the heating of kaolin, which was the object of KLEVER's paper, is of little direct interest here. However, his results are an indication of the accuracy of his measurements, and are reproduced in Fig. 1. It is apparent that the curves correctly reflect the well-known structural changes which occur in kaolin at about 550° and 900°C. The configuration of the heat of solution curve is actually due to structural change, and not merely to water content, because the heat of solution of water is negligible (see above).

From the continuity of the curves above 550°C, KLEVER concluded that there is no structural breakdown of kaolin at this point, as some investigators had assumed. Rather, there was felt to be support for the existence of a new compound, "metakaolin." This had been suggested by a number of other workers, from X-ray data (e.g., HYSLOP, 1926). The assumption that metakaolin exists has been criticized by EITEL (1941) and by SOSMAN (1933). EITEL concludes that there is no basis for assuming the existence of such a compound. It is not necessary to take sides on this question, but in general support of the accuracy of KLEVER's work, it should be noted that recent work by COMEFORO (1948) tends to substantiate the existence of metakaolin.

Table 7. Standard enthalpy change for certain silicate reactions

No.	*Reactants*	*Products*	$-\Delta H$ (kcal)	*References*
		A		
1	$Al_2O_3 + SiO_2$ (alumina, quartz)	Al_2SiO_5 (sillimanite)	44·4	Rossini (1952)
2	$CaO + SiO_2$ (lime, quartz)	$CaSiO_3$ (wollastonite)	27·7	Bichowsky (1936)
3	$K_2O + Al_2O_3 + 6SiO_2$ (potash, alumina, quartz)	$2KAlSi_3O_8$ (adularia)	117·9	Mulert (1912)
4	$K_2O + Al_2O_3 + 6SiO_2$ (potash, alumina, quartz)	$2KAlSi_3O_8$ (microcline)	90·9	Mulert (1912)
5	$Na_2O + Al_2O_3 + 4SiO_2 + H_2O$ (soda, alumina, quartz, water)	$2NaAlSi_2O_6 . H_2O$ (analcite)	76·4	Mulert (1912)
6	$CaO + Al_2O_3 + 6SiO_2 + H_2O$ (lime, alumina, quartz, water)	$CaAlSi_6O_{12} . 5H_2O$ (heulandite)	46·2	Mulert (1912)
		B		
7	$CaO + H_2O$	$Ca(OH)_2$	16·0	Bichowsky (1936)
8	$Na_2O + H_2O$	$2NaOH$ xal.	36·3	Bichowsky (1936)
9	$Na_2O + H_2O$	$2NaOH (\infty H_2O)$	56·8	Bichowsky (1936)
10	$Al_2O_3 + 3H_2O$	$2Al(OH)_3$	9·7	Bichowsky (1936)
11	$CaO + CO_2$	$CaCO_3$ (calc.)	43·3	Bichoswky (1936)
12	$K_2O + H_2O$	$2KOH$ xal.	48·8	Bichowsky (1936)
13	$K_2O + H_2O$	$2KOH(\infty H_2O)$	75·3	Bichowsky (1936)
		C		
14	$2Al(OH)_3 + SiO_2$ (quartz)	$Al_2SiO_5 + 3H_2O$ (sillimanite)	34·7	Above
15	$Ca(OH)_2 + SiO_2$ (quartz)	$CaSiO_3 + H_2O$ (wollastonite)	11·7	Above
16	$2KOH + 2Al(OH) + 6SiO_2$ (xal., quartz)	$2KAlSiO + 4HO$ (adularia)	59·5	Above
17	$2KOH + 2Al(OH)_3 + 6SiO_2$ (∞H_2O, quartz)	$2KAlSi_3O_8 + 4H_2O$ (microcline)	6·0	Above
18	$2NaOH + 2Al(OH)_3 + 6SiO$ (∞H_2O, quartz)	$2NaAlSi_2O_6 . H_2O$ analcite$+2H_2O$	10·0	Above
19	$CaCO_3 + SiO_2$ (calcite, quartz)	$CaSiO_3 + CO_2$ (wollastonite)	−51·6	Above
		D		
20	$H_4Al_2Si_2O_9$ (kaolinite)	$Al_2SiO_5 + 2H_2O$ (sillimanite) + SiO_2 (quartz)	26·0	Klever (1930)

COMEFORO, using X-ray analysis and electron microscopy, concludes that there is evidence for the existence of "a uniquely organized, non-crystalline compound for which the name meta-kaolin or pro-mullite seems fully justified."

From the curves, the following heats of reaction are obtained:

1. $2H_2O + Al_2O_3 + 2SiO_2 \rightarrow H_4Al_2Si_2O_9 +$ 22,000 calories.
2. $Al_2O_3 + SiO_2 \rightarrow Al_2SiO_5$ (sillimanite) + 48,000 calories.
3. $H_4Al_2Si_2O_9 \rightarrow Al_2SiO_5 + 2H_2O + SiO_2 +$ 26,000 calories.

The value 1 above is in fair agreement with the value 18 kcal/mole obtained by SCHWIERSCH (1939) and the value 2 is in good agreement with the corresponding value listed by ROSSINI (see Table 7)

Superposed on the reaction effect is the effect of surface energy, which was not considered by KLEVER. As a first approximation, this effect may be ignored, which assumes that the fineness affects all particles similarly. If the fineness of all particles were the same, the heat of solution of the harder silicates (relative to the heat of solution of coarse material) would be expected to be increased more than the heat of solution of the softer ones. The heat of reaction 3 would then be even higher than listed. If the kaolin is the finer material, then the greater surface might counterbalance this effect. All in all, the best course at present is to ignore the surface effect when writing the values. In further experimental work of this sort, the surface and strain energy should be considered.

Assuming adiabatic conditions, the above value for the reaction:

$$\text{Kaolin} \rightarrow \text{sillimanite} + \text{quartz} + \text{water}$$

gives a temperature *rise* of about 340°C. This includes the water as a product, but does not consider latent heat effects of the latter. The water would be above its critical pressure in most cases. If the effect of water is neglected—and this assumes that it eventually reaches the surface at surface temperature—the adiabatic rise is about 420°C.

Summary

The above data indicate that a number of important anamorphic changes are exothermic. Thus there is no doubt of the exothermic effect of devitrification. This phenomenon is of small importance in metamorphism, however, and the heat source is not "primary," because some earlier energy within the crust was necessary to produce the glass. There is also no doubt of the exothermic effect of recrystallization, and this process is of the most widespread importance in metamorphism. The ultimate source of this energy is believed to be the sun, as will be indicated below.

Concerning reactions, the "exothermic" case is not so clear, and at least some minor reactions are endothermic. However, most of the important reactions appear to be exothermic, and certainly the onus of proof is with those who would presume the contrary. Again, the source of the chemical energy is believed to be the sun.

The most significant feature of the data is the magnitude of the energy concerned, as shown by the adiabatic temperature rise calculations. These indicate that adiabatic temperature rises of a few hundreds of degrees are possible in chemical reactions, and it must be that recrystallization heat will make these values even higher.

The "adiabatic" condition is an ideal one, and in every natural case an interplay of heat production and dissipation would occur. This is mentioned in Section II. What is certain is that anamorphic reactions *do* occur, and in finite time, so that *some* heat effect must result. Better data on reaction rates and heats, and more detailed mathematical analysis, are required to give the complete picture.

In the following section, some additional evidence for the sign of the metamorphic heat effect is presented.

B. Indirect Evidence Concerning the Sign of the Heat Effect in Metamorphism

Indirect evidence of the sign of the heat effect in metamorphism is provided by thermodynamics, and also by study of the energy economy of the earth.

(i) *Thermodynamics*

For the change

$$A \rightarrow B$$

to occur, the associated change in GIBB'S free energy (ΔF) must be negative. Therefore, considering a closed system, the relation

$$\Delta F = \Delta H - T\Delta S \qquad (1)$$

indicates that, if the change occurs, ΔH must in general be negative. An endothermic reaction (positive ΔH) can occur spontaneously only if the entropy change (ΔS) for the reaction is positive, and then only if the product $T\Delta S$ is greater than ΔH.

Now, in anamorphism (again considering closed systems) it is obvious that the general tendency is towards decrease in entropy. For example, the clays and colloids of muds and shales are much more random, shambling structures than their chemical equivalents in feldspar, mica, amphibole, etc. If addition solid-state reactions occur, because ΔS is almost zero for these, ΔH would have to be negative for reaction to occur. In this connection, see TAMMANN (1925).

Even if ΔS is positive, the values concerned in many anamorphic reactions are such that the factor $T\Delta S$ is unlikely to approach ΔH in magnitude at temperatures much below that of fusion. Data on entropy changes in silicate reactions are scarce, but the entropy change at fusion may be taken as an approximation. This approximation probably gives too high a value for ΔS, but even when using it the above statement concerning the magnitude of $T\Delta S$ is generally true.

If ΔH for an endothermic reaction is sufficiently small, the reaction may be spontaneous in a closed system, provided that ΔS for the reaction is positive. This is obvious from equation (1). On this basis, the spontaneous aragonite-calcite transition (see Table 5) is not anomalous. The higher density of aragonite indicates that it has the lower entropy, which is in harmony with the above.

It is, therefore, probable that closed-system anamorphic reactions are exothermic. Concerning open systems, the relations are less straightforward. Nevertheless, it can be shown that the concept of exothermic anamorphism is compatible with geologic observation, and that it is probably valid.

In the case of open systems, removal of mass may permit reactions for which, in closed systems, ΔF is positive or zero. (A familiar example of the latter is the displacement of reaction equilibrium by product removal, as described by LE CHATELIER'S principle.) Therefore, observed spontaneity of open-system changes does not by itself give unequivocal information about the associated enthalpy changes. This is evident when the reactions of authigenesis and weathering are considered. In many cases, these involve the same minerals, and the temperatures and pressures obtaining in the two environments are not essentially different, yet the reactions proceed in opposite senses. Both sets of reaction cannot, of course, be exothermic. However, the situation is in no sense anomalous, and is the result of certain differences in the systems, which can be shown as follows:

Consider the change:

$$\text{CLAY} + \text{CATIONS (Adsorbed, in solution)} \rightarrow \text{FELDSPAR} + \text{WATER}$$

or, abbreviating,

$$C + I \rightarrow F + W,$$

for which the change in free energy at standard conditions is ΔF^0. Then we have that

$$\Delta F^0 = -RT \ln K$$

where R is the gas constant, and K the equilibrium constant of the reaction. Now K may be written approximately

$$K = \frac{(F)(W)}{(C)(I)},$$

where the brackets indicate concentration. Therefore we have:

$$\Delta F^0 = RT \ln \frac{(C)(I)}{(F)(W)}$$

From this it is evident that, even if ΔF^0 for the reaction

$$C + I \rightarrow F + W$$

is strongly negative for the clay environment, and feldspar thus the favoured form, the ratio $(C)/(F)$ may nevertheless be large, provided that the ratio $(I)/(W)$ is kept sufficiently small. In weathering, this is just the tendency that is operative. Therefore, the evidence of weathering reactions is not incompatible with spontaneous authigenic growth. The efficacy of cation removal in accelerating weathering of feldspar has been shown experimentally by NORTON (1937).

It might be argued that this reasoning would apply equally well in the reverse sense—that is, to show that feldspar growth can occur even though the closed-system tendency is greatly in favour of the clay state. However, this "driving" of a reaction against a closed-system free energy tendency can be achieved only by input of energy. At the surface, this energy, required to transport cations from the feldspar crystal, and hence undermine its cohesion, is clearly available, in the mechanical and thermal energy of running water. There is, moreover, no limit to the extent to which the reaction can be driven towards the clay side. That is, the factor $(I)/(W)$ can become indefinitely small. In authigenesis, there is certainly the tendency towards mechanical expression of water from the clay mass, and the adsorption of cations on the clay surface. The driving force here is the gravitational pressure gradient. However, this force cannot be so efficient as that

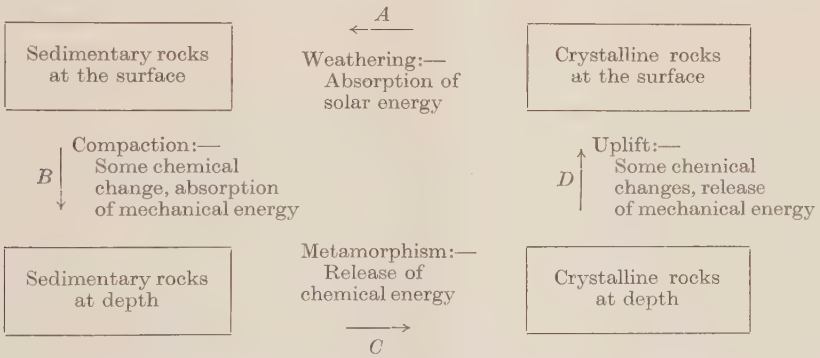
which drives the surface weathering reactions. Neither can it operate to form feldspar for an indefinitely long period. For, eventually, further removal of water by pressure alone will become impossible, and the system becomes effectively closed.

Further reaction can then occur only in accordance with the principles expressed earlier. There are not sufficient data available to solve the complicated problem of just how much feldspar would be in equilibrium with clay at this dehydration limit (assuming positive ΔF^0 for the reaction). In the writer's opinion, the amount would be small. Certainly, it is difficult to conceive of such an authigenic mechanism proceeding to the limit of a "granitization," and yet observation suggests that there is every gradation between these two anamorphic extremes.

(ii) *Terrestrial energy economy*

It is the opinion of the writer that the energy economy of the earth as a whole and the geologic cycle, are much more intelligible if exothermic "regional metamorphism" is assumed.

Consider the following scheme for the geologic cycle of change:


A
Sedimentary rocks at the surface
Weathering:— Absorption of solar energy
Crystalline rocks at the surface
B
Compaction:— Some chemical change, absorption of mechanical energy
D
Uplift:— Some chemical changes, release of mechanical energy
Sedimentary rocks at depth
Metamorphism:— Release of chemical energy
Crystalline rocks at depth
C

magnitude of energy A approximately = magnitude of energy C

magnitude of energy B approximately = magnitude of energy D

Σ energies = $(A + B + C + D)$ approximately = 0.

This cycle differs from the usual one in the steps A and C, and hence in the hypothesis that the cycle is essentially self-sustaining. That is, no major influx of energy from "below" is assumed, although such influx is not precluded. The ultimate driving force of the cycle is solar energy, transmitted to the surface rocks mechanically and chemically, and carried to depth in the thermodynamically unstable rock product. The kinetic factor makes this burial possible, as will be outlined in the following sections.

The role assumed to be played by solar radiation is not incompatible with meteorological fact, or at least the writer is not aware of any such incompatibility. Solar energy is certainly of the correct order of magnitude to account for the various orogenic and anamorphic processes provided it is properly trapped and utilized.

Given that there is a net influx of solar energy over any normal year, it follows that surface

processes are, on the whole, endothermic, if geologic climate has been even approximately constant. Meteorological studies of this point do not appear to offer much of a positive nature. The processes concerned are extremely complex, and there is an insufficiency of data even on those processes which are relatively well understood. The present meteorological approach is to assume that the earth is in radiative equilibrium with the sun. See, for example, SIMPSON (1929). Internal storing of solar energy is not considered, but a consistent energy scheme could be built up which would incorporate the principle of endothermic surface processes.

Certain surface processes are without doubt endothermic. These are mechanical fracturing and comminution of material, and animal and vegetable growth, where this is entombed (i.e., in coal, and in oil formation). Normal weather processes are cyclic, and contribute nothing. Most of the processes associated with our present technology are exothermic. However, these are of recent origin, and all the energy released (possibly excepting that from atomic sources) is ultimately solar. These points are mentioned to emphasize that the meteorological picture of a chemically inert earth cannot be entirely correct.

From the above, it is obvious that the problem of the chemical energy variation in metamorphism is but one part of the broader problem of the chemical energy change in geological processes generally. The present paper is devoted primarily to the metamorphic problem, because it is with respect to this problem that the present ideas have most direct geologic significance, and can be most directly tested.

II. KINETICS

No matter what the sign of the heat release in regional metamorphism, it is certain that there is *some* heat effect. One can dismiss the possibility that the heats of exothermic and endothermic reactions just balance each other, because this could not occur throughout all stages of the metamorphism. (It might occur for a certain time period, or through a certain small space.)

Given the enthalpy change data, a dynamic picture of the chemical heat effects requires knowledge of the kinetics of the processes involved—that is, the kinetics of the chemical energy release, and of its subsequent distribution according to the laws of heat flow in the region of interest.

A. Kinetics of Chemical Change

Readers unfamiliar with this subject are referred to the excellent treatment of GLASSTONE *et al.* (1941). Solid state reactions deserve special attention by the geologist, because the *general* solidity of the environment of metamorphic reactions cannot be doubted. For a review of the subject of solid state reactions see HEDVALL (1937).

Present knowledge of the kinetics of chemical change does not permit the writing down of simple, definite values for the rates of metamorphic reactions, even if the necessary data were available. Rocks are, in detail, extremely inhomogeneous bodies, and it is to just such inhomogeneities as rocks display, that reaction rates are most sensitive.

For this reason, the writer has not attempted to collect numerous values for reaction rates of geologic materials. Representative values are given in part *C*, below.

B. Kinetics of Heat Flow

Assuming that we know the rate parameters of the chemical sources and sinks within a certain region, we can know the temperature at each point if we know the heat flow parameters of the region, and the initial and boundary conditions. In practice, this is a difficult problem and generally defies analysis.

Here, only a qualitative picture is necessary. One must imagine the interplay of reaction heat and heat transfer: at any particular point, a certain chemical reaction proceeds at a certain rate, which is primarily dependent upon the ambient temperature. This reaction will release or absorb a certain quantity of heat in a given time interval. After this interval the temperature of the elemental volume will have changed according to the laws of heat transfer which are operative. Within the elemental volume there is now less reactant. During the next time interval, the process will continue in a similar way. There are obviously a multitude of temperature-space-time relations possible, depending upon reaction heat, rate, initial conditions, ... One of the most interesting types of behaviour is that in which heat production exceeds heat transfer for some time interval, and this is discussed in the next section.

Thermal autocatalysis

That process, in which a reaction alters the temperature of its environment, and hence the velocity of subsequent reaction, may be termed thermal autocatalysis. This condition may arise for either endothermic or exothermic reactions, but only for exothermic reactions is there the possibility of an increasing rate of change of temperature.

Fundamentally, thermal autocatalysis must occur in every case where the rate of establishment of thermal equilibrium is less than the rate of heat production or absorption by the reaction. On this basis, the effect is probably of wider occurrence than is usually recognized. In non-violent cases, it would be difficult to detect simply.

Thermal explosions in gases must be initiated suddenly, as a result of a strong stimulus towards reaction: e.g., a spark. This is because of the relatively high efficiency of heat transfer in gases.

However, in material in which heat flow is less efficient, such as in certain solids, reactions are able to begin catalysis with much less sharp stimuli. For the same reason, reactions in such material may show much longer induction periods. Examples of long induction periods of this sort are common in cases of spontaneous combustion—such material as coal or oily rags may smoulder for many months before igniting.

These topics are significant for geology, because, although many geologic reactions are extremely slow, the rate of heat transfer in rock materials can be correspondingly slow. Therefore, for exothermic reactions, thermal autocatalysis must always be considered as a possible accelerating device. This is particularly true for slow reactions, because these reactions have a large activation energy, and therefore their rates show very great temperature dependence.

C. Experimental Data

The following values have been determined from work on:

(i) Single interfaces between solids,

(ii) Mixture of powders,

(iii) Geologic data.

For additional values, see JOST (1936), and HEDVALL (1937).

(i) *Single inference reactions*—A large number of reactions have been studied with the reactants in the form of slabs pressed together. In these cases, once reaction has begun, succeeding reaction can only take place by diffusion of the reactants through the product layer. JAGITSCH (1946) studied the reactions ($MgO + Ag_2SO_4$), ($MgO + Ag_3PO_4$), ($MgO + Mg_2P_2O_7$), and ($MgO + MgSiO_3$) in this manner, and found that the rate of reaction was independent of the thickness of the product layer. He was able to express his results in the form:

$$\frac{dm}{dt} = Ce^{-Q/RT}$$

where dm/dt is the rate of reaction in gram-moles of MgO per sq cm of contact per sec, and C, Q are constants. The results are given in Table 8.

Table 8. Rates of single-interface solid-state reactions
(JAGITSCH, 1946)

Rate expression: $dm/dt = Ce^{-Q/RT}$

No.	*Reaction*	Q (kilocalories)	C g-mol . MgO cm^{-2}/sec^{-1}
1	$MgO + Ag_2SO_4$	61	$2{\cdot}0 \times 10^5$
2	$MgO + Ag_3PO_4$	61	$2{\cdot}0 \times 10^5$
3	$MgO + Mg_2P_2O_7$	82	$2{\cdot}0 \times 10^5$
4	$MgO + MgSiO_3$	112	$1{\cdot}0 \times 10^5$

(ii) *Mineral powders*—Determination on mixtures of powders are of more direct geologic significance than are the above type. As would be expected, rates depend on particle size, and intimacy of contact. JANDER (1937) has developed the mathematical relation between particle size and reaction rate. His equation does not apply to slow reactions. For these, SEGAWA (1949) has calculated a corresponding relation, by assuming that the rate is entirely diffusion-controlled. The final form obtained by him may be written:

$$\frac{dx}{dt} = K(1 - x)^n$$

where

$$K = Ae^{-Q/RT}$$

Here, X is the fraction of the material reacted at time t, and A, n are constants.

On the basis of this theoretical analysis, SEGAWA calculated the reaction rates of numerous reactions between powders, from differential thermal analysis data. A few of the values obtained are listed in Table 9.

(iii) *Geologic data*—In some cases, geologic occurrences can provide data on reaction rates, if enough is known of the geologic history. As an illustration of this, consider the data given by Moore (1952) on authigenic feldspar in the Green River shale.

Table 9. Reaction rates from thermal analysis of mineral powders (Segawa)

Rate expression: $dx/dt = K(1-x)^n \qquad K = Ae^{-Q/RT}$

No.	*Reaction*	K (1/*sec*)	Q (*kcal/mole*)
5	$CaO + SiO_2$	—	71·2
6	$CaSiO_3 + CaO$	—	61·1
7	$Al_2O_3 + SiO_2$	—	40·0
8	$MgO + Fe_2O_3$	$10^{12\cdot86}$	75·3
9	$CrO + Fe_2O_3$	$10^{14\cdot6}$	84·3

Moore states that the maximum length of the rhomb-shaped crystals is about 3 mm (measured on the diagonal) and the average length about 0·15 mm.

Now, if we assume a rate of the form

$$\frac{dm}{dt} = Ce^{-Q/RT}$$

where dm/dt is the number of moles reacting per unit time per unit volume, and C, Q are constants, we have approximately

$$\frac{\Delta m}{\Delta t} = Ce^{-Q/RT}$$

This of course assumes constant temperature, and the form of the rate ignores the effect of disappearance of mass.

Assuming that the crystals are in the form of rectangular parallelepipeds, then it is easily computed that:

(a) For the maximum size crystal: $m = 3 \times 10^{-5}$ mole/unit vol.

(b) For the average size crystal : $m = 4 \times 10^{-9}$ mole/unit vol.

Now, the Green River formation is Middle Eocene, and taking its age as sixty million years, the elapsed time is approximately 2×10^{15} sec. It is now necessary to estimate values of Q and T, in order to compute C. These estimates, together with the resultant values of C, are given in Table 10 below. The results show, primarily, the sensitivity of the computations to changes in Q and T, and no particular best choice is suggested. Rather, the point that, *with reasonable assumptions, a very large range of values of C is possible.*

In calculating C above, the "unit volume" has been taken as 1 c.c. This may be excessive, as far as the actual occurrence is concerned, but the calculation of C is not so sensitive to the choice of unit volume, or to the assumption of crystal size, as it is to choice of Q and T. This is apparent from the tabulated results.

D. Discussion

It has been mentioned above that the problem of the temperature and amount of reaction in a region containing chemical sources is a complicated one, for which an analytic solution is not at present available. Numerical methods might be used to give information on particular cases, but the enthalpy change data for geologic

Table 10. *Approximation of the frequency factor from data on authigenic albite*

No.	$\frac{\Delta m}{g\text{-}mol/cm^3}$	Δt *sec*	$\frac{\Delta m/\Delta t}{g\text{-}mol/cm^3\ sec}$	T°C	T°K	$\frac{Q}{kcal/mole}$	C *text*
10	3×10^{-5}	2×10^{15}	$1{\cdot}5 \times 10^{-20}$	127	400	40	$1{\cdot}5 \times 10^{1{\cdot}5}$
11				77	350	40	$1{\cdot}5 \times 10^{5}$
12				27	300	40	$1{\cdot}5 \times 10^{8}$
13				127	400	60	$1{\cdot}5 \times 10^{12}$
14				77	350	60	$1{\cdot}5 \times 10^{17}$
15				27	300	60	$1{\cdot}5 \times 10^{23}$
16				127	400	80	$1{\cdot}5 \times 10^{23}$
17				77	350	80	$1{\cdot}5 \times 10^{29}$
18				27	300	80	$1{\cdot}5 \times 10^{37}$
19				127	400	100	$1{\cdot}5 \times 10^{34}$
20				77	350	100	$1{\cdot}5 \times 10^{42}$
21				27	300	100	$1{\cdot}5 \times 10^{52}$

For the smaller crystals, $m = 4 \times 10^{-9}$ mole/vol, and C is $4/3 \times 10^{-4}$ of that given above.

reactions, and particularly the rate data, are in many cases too poor to justify much labour in this direction. (Sets of calculations for various parameters would, of course, be useful.)

In connection with the present paper, the most obvious question relating to kinetics is whether thermal catalysis, as described above, is likely to occur at all. To obtain a rough idea, one may use the existing rate data, and calculate the temperature which would be required to make reaction heat equal the observed terrestrial heat flow, as follows.

For any given cubic centimetre of rock, per unit time, there will be an amount of heat flowing in from below, and another amount flowing out at the top. It is assumed that there is no flow out of the sides. If there are no sources, and there is equilibrium, then these amounts are equal.

Table 11. *Temperature at which reaction heat/cm³ equals terrestrial heat flow/cm²*

Reaction No.	*Table No.*	$-\Delta H$ *in kcal/mole*	Q *kcal/mole*	T°C
4	8	10	112	850
8	9	10	75	520
11	10	10	40	320
14	10	10	60	200
17	10	10	80	165
20	10	10	100	140
21	10	10	100	75

Here, the incoming heat flow is disregarded, and it is required that reaction heat just equal the outgoing heat, which is taken to be one microcalorie per sq cm per sec. The results obtained, using some of the reaction rates of the previous section, are tabulated below. The values are orders of magnitude only.

The temperature calculations are most sensitive to changes in the value used for the activation energy, and much less sensitive to changes in ΔH, or in the frequency factor.

In this connection, it should be recognized that the actual geologic environment is a heterogenous one, in which there are many places where the required activation energy is considerably less than average; for example, in strained or disordered crystals, along grain boundaries, close to radioactive minerals, or where there are mobile phases. Local areas of lowered or even reversed heat flow also exist in the geologic environment, and will likewise affect matters. Therefore, the results of Table 11 indicate that thermal catalysis is a possibility, if the rate data used are even approximately correct. Also, the data suggest that thermal autocatalysis will be a sort of borderline case, which may or may not occur, depending upon local conditions. This would be compatible with geologic observation.

Some additional numerical examples of the effect of changes in temperature and activation energy on reaction rate are useful in evaluating the present possibilities. These are given in Table 12.

Table 12. *Numerical examples of the effect of changes in temperature and activation energy on the rate constant*

Form of the rate constant: $k = Ae^{-Q/RT}$

1. $Q = 100{,}000$
   Changing T from 300°K to 305°K increases k 16 times.
   Changing T from 300°K to 400°K increases k $6{\cdot}5 \times 10^{35}$.

2. $T = 300$°K.
   Decreasing Q from 100,000 cal/mole to 99,000 cal/mole increases k 5 times.
   Decreasing Q from 100,000 cal/mole to 95,000 cal/mole increases k 3800 times.

3. For a first-order reaction, and constant temperature, the fraction of material reacted at any time t after the start of the reaction is:

$$\text{Fraction reacted} = 1 - e^{-kt}$$

   Two examples of fraction of reaction as related to different values of t and T are:

	Q (*cal/mole*)	T (°C)	t (*yrs*)	*Fraction reacted*
(a)	100,000	400	1×10^9*	0·1
(b)	100,000	410	2×10^7*	0·9

* These times (a) and (b) correspond roughly to the times elapsed since the Pre-Cambrian and the Tertiary, respectively. Note that, owing to the different values of T, the "younger" reaction is the more nearly completed.

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ANNOUNCEMENTS

LETTERS TO THE EDITORS

The Editors invite brief communications for publication in this Journal under the heading of "Letters to the Editors." It is intended that this should provide an opportunity for critical comment on geochemical and cosmochemical topics and for rapid publication of preliminary results, where this is desirable. This Journal is now publishing two volumes per year, with an average of one issue per month. Letters to the Editors can therefore be published without delay. The length of these letters should, if possible, not exceed 500 words.

FOURTH NATIONAL CLAY CONFERENCE

The Fourth National Clay Conference will be held at University Park, Pennsylvania, from 10 to 13 October 1955. In connection with The Pennsylvania State University Centenary, arrangements have been made to have several scientists from Europe and Asia attend and present papers. Further information can be obtained from the Chairman of the Local Committee: Professor T. F. BATES, 315 Mineral Sciences Building, University Park, Pennsylvania.

IN MEMORIAM

JOHN PUTNAM MARBLE (1897–1955)

The Division of Earth Sciences, National Research Council, Washington, D.C., announces with great regret the sudden death on 6 June 1955 of Dr. JOHN PUTNAM MARBLE, chairman of the Committee on the Measurement of Geologic Time and principal editor and compiler of this Committee's annual report. Dr. MARBLE's death is not only a personal loss to his friends; it is also a great professional loss to the many users of the reports of his committee.

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